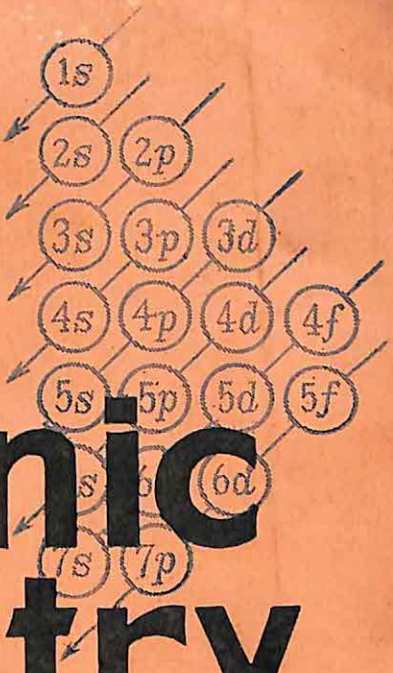
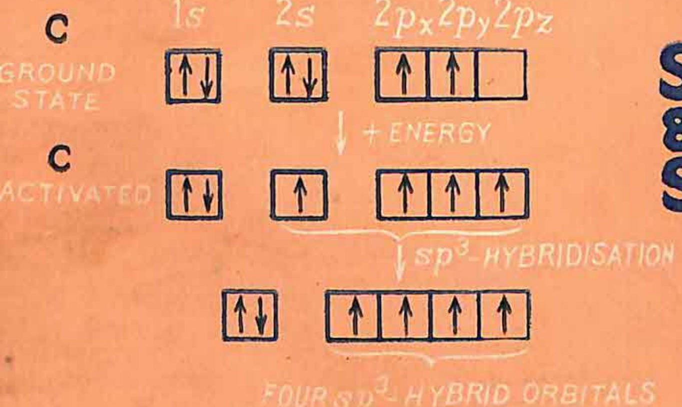
General & Inorganic Chemistry





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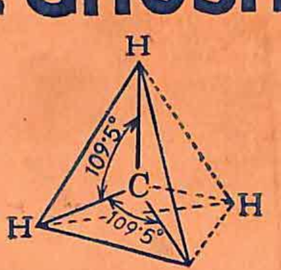

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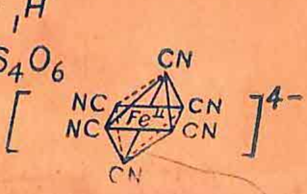
$${}_7N^{14} + {}_2He^4 \longrightarrow [{}_9F^{18}] \longrightarrow {}_8O^{17} + {}_1H^1$$

$$I_2 + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6$$

$$Fe(CN)_2 + 4KCN = K_4[Fe(CN)_6]$$



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GENERAL & INORGANIC CHEMISTRY

A TEXT BOOK FOR B.Sc. STUDENTS

VOLUME II

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A FEW WORDS ABOUT THE BOOK

To cater the needs of the students in a much better way, we decided to reorganise and recast the entire subject-matter of this volume in the light of the recent trends in the questions set for the examinations of the different Universities. Such an elaborate change demands much effort on our part and the time factor involved is of considerable magnitude. So, in order to meet the immediate demand, we have decided to reprint the present edition for the time being, after carefully correcting the errors and printing mistakes and leave the elaborate revision for the next edition. We do hope that the teachers and the students will bear with us the inconvinience caused for the present.

AUTHORS

Dated, Calcutta
29th March, 1988.

PREFACE TO THE FIRST EDITION

This book covers the B.Sc. (pass) course syllabi of most of the Indian Universities. It particularly covers the entire syllabi of general and inorganic chemistry of all the Universities of Eastern India. In the recent years, the under-graduate inorganic chemistry syllabi of all the Indian Universities have undergone a radical change, and at present, there exists very little difference between the B.Sc. pass level and the corresponding honours course. This has made the writing of a text book on **general and inorganic chemistry** for the B.Sc. pass course a challenging task which necessarily required a simple and very lucid exposition of the comparatively difficult and complicated topics of general chemistry and descriptive inorganic chemistry, so long reserved for the more meritorious and much more serious students taking up the honours course.

The book is divided into **Part I** and **Part II.** Part I begins with an "Introduction" which serves as a logical link between the Higher Secondary course and the new degree syllabi. The rest of the part I includes the important fundamental principles of general chemistry, spanning chapters I—VII. The discussions of these principles are illustrated with adequate diagrams and figures, and abound in relevant examples from inorganic chemistry along with numerical examples wherever essential. The remaining portion of part I deals with the chemistry of the periodic groups O, IA, IB, IIA, IIB and IIIA. The **Appendix** of this part deals with relevant numerical problems illustrating the fundamental principles.

The part II of this book contains the descriptive inorganic chemistry of the elements of the rest of the periodic groups included in the syllabi, written on the basis of their electronic configuration, position in the periodic table and the influence of the physical factors like atomic and ionic radii, ionization potential and electron affinity, electronegativity, the nature of the bonding involved etc. A preliminary idea of the more important characteristics of the inorganic solids, along with the basic principles of crystallography, is essential and useful, and these are included in the Appendix of Part II which also includes a large number of model questions (both objective and subjective), covering the subject-matter of the entire book.

We sincerely hope that this book will meet the requirements of the students and teachers, generated as a result of the introduction of the new syllabi. We had to write this book rather hurriedly, as a result of which some minor errors and inadequacies might have crept in and for which the responsibility is entirely ours.

All criticisms and suggestions about this book will be thankfully received and gratefully acknowledged.

Dated, Calcutta
25th November, 1980.

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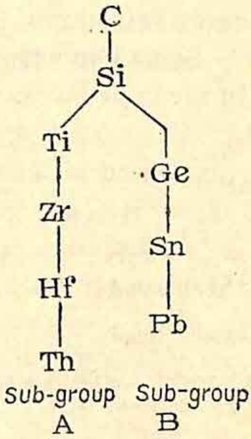
CHAPTER XV

ELEMENTS OF GROUP IV B

The fourth group of the Periodic Table contains altogether nine elements, and as is usual in the previous groups, they are sub-divided into two sub-groups, *viz.* IV A and IV B. The sub-group A consists of the elements titanium, zirconium, hafnium and thorium, which are *transitional elements*, the element thorium being radioactive in addition. The sub-group A, on the other hand, comprises five elements, *viz.* carbon, silicon, germanium, tin and lead, and this is the main sub-group of Group IV. Of the five elements in this sub-group, germanium is less familiar and is available only in small quantities in nature. We will, therefore, restrict our discussion in this chapter mainly in the chemistries of carbon, silicon, tin and lead.



Although the elements in each sub-group have certain similarities among themselves, those of the two sub-groups have barely any striking resemblance among them, except their principal valency of four units and the not-too-pronounced electropositive or electronegative character. In fact, the following contrasts among the members of the two sub-groups are quite apparent: (i) The valence-shell electronic configuration of the elements of sub-group A is $(n-1)d^2ns^2$, while that of the elements of sub-group B is ns^2np^2. This is responsible for the existence of the elements of the former sub-group in the oxidation states of +2, +3 and +4, while the elements of the latter sub-group exhibit mainly tetravalency and divalency. (ii) The metals of the sub-group A have very high melting points, while those of the sub-group B melt at comparatively much lower temperatures. (iii) The hydrides of the elements of the sub-group A are solid, while those of the elements of sub-group B are generally gaseous. (iv) The chlorides of the elements of the sub-group A are all solids (except $TiCl_4$, which is a liquid), while the chlorides of the elements of the sub-group B are mostly liquids.

General Characteristics of the elements of Group IV B (Carbon, silicon, tin and lead).

All the four elements, *viz*. carbon, silicon, tin and lead are relatively familiar ; silicon, among them, constitutes about 27·7% of the earth's crust (as silica and mineral silicates), while tin and lead are less abundant than many of the so-called rare-elements. In nature, carbon is found in more compounds than all the other elements combined, especially in large quantities in the plant and animal kingdoms.

Some important physical properties of these elements are given in the table below :

TABLE 15·1

Property	Carbon	Silicon	Tin	Lead
Atomic number	6	14	50	82
Atomic weight	12.01	28.06	11.87	207.2
Electronic configuration of outermost shell	$2s^22p^2$	$3s^23p^2$	$5s^25p^2$	$6s^26p$
Density (20°C), g/c.c.	3.52 (Diamond) 2·25 (Graphite)	2.35 (amorph.) 2.5 (cryst.)	7.3	11.36
Atomic volume (c.c.)	3·4 (Diamond)	11·4 (cryst.)	16·3	18·2
Covalent radius (Å)	0·77	1·11	1·41	1·44
Melting point (°C)	3500	1420	231·8	327·3
Boiling point (°C)	(4200)	2600	2260	1620
Ionisation potential (ev)	11·264	8·149	7·32	7·415
Electronegativity	2·5	1·8	1·8	1·8
Heat of sublimation kcals/gm.	*ca.* 170	85	78	47·5

All the elements of this family (carbon family, as it is called) show some amphoteric character which is in accordance with their position between the electropositive elements of Groups I, II and III in the left and the electronegative elements of Groups V to VII towards the right. Nevertheless, the trends in changes from non-metallic to metallic behaviours of the elements with the increase of their atomic weights are very pronounced. Carbon and silicon, being the members of the two short periods of the Periodic Table, are the *typical elements* of this group. Carbon is definitely a non-metal; silicon is usually considered as a non-metal, although it possesses some metallic properties; but, tin and lead are true metals. These trends are, of course, associated with the reduced effective nuclear charges and increased sizes of the atoms.

The very small atomic volume and the considerably high electronegativity of carbon are responsible for certain uniqueness of this element. No other element forms so numerous compounds as carbon and, in fact, organic chemistry is actually the chemistry of carbon compounds.

Catenation or self-linkage: Atoms of carbon can combine with one another to form long chains or rings, the bond between two adjacent carbon atoms may be single, double or triple (for the description and significance of carbon-carbon double and triple bonds, see Volume I, pp. 158). It can also bind itself with other elements like hydrogen, nitrogen, sulphur, halogens *etc.* Silicon shares such properties to a smaller extent, but no other element possesses such characteristics.

The melting and boiling points of the members of this family of elements decrease with the increase in atomic weights and the density increases with increasing atomic weights.

Valency and oxidation state: All the four elements exhibit tetravalency; tin and lead (as also carbon in carbon monoxide) show valency of two units also. The ionisation potentials of these elements are very high and, as such, the existence of simple tetrapositive ions (M^{+4}) is unlikely. The electronegativity values are also low (and they do not decrease in a completely regular way); the tetranegative ions (M^{4-}), therefore, do not exist normally, although carbon forms C_2^{2-} ions in salt-like carbides like CaC_2. The elements all show a covalency of 4, which necessitates promotion of electrons from the ground state to an exited state, and sp^3 hybridisation of the orbitals results in a tetrahedral structure (see volume I, chapter III, pp 155-56).

These valency characteristics of the elements are in accordance with the electronic structure of their atoms, which consists of 4 electrons in the outermost (valence) shell with a stable core of 2, 8 or 18 electrons. These four electrons comprise two pairs in *s*- and *p*- orbitals of the *n*th shell. Either one or both of these pairs of electrons may be utilised for bonding. In case only one pair is effective, the other pair remains as the *inert pair*, and divalency of the element results. It is the two *ns* electrons that form the inert pair. The effect of the inert pair of electrons is most pronounced in the element with the highest atomic weight, *i.e.* lead. Thus, there is a decrease in stability of +4 oxidation state and an increase in the stability of +2 oxidation state as the atomic number increases (*i.e.* on descending the group). The lower valencies are more ionic because the radius of M^{+2} ig greater than M^{+4} (*cf.* Fajans' rules, *viz.* the smaller the ion and greater the positive charge on it, the greater the tendency to covalency). Thus, Sn^{+2} is ionic (but strongly reducing) and Sn^{+4} is covalent ; Pb^{+2} is ionic, stable and more common than Pb^{+4} which is strongly oxidising.

Allotropy : All the elements of this sub-group (except lead) exhibit allotropy. Carbon exists in crystalline (diamond and graphite) and amorphous (charcoals, lampblack) allotropic modifications ; silicon exists in crystalline and amorphous forms, but they are not true allotropes, as amorphous silicon is also composed of minute octahedral crystals like the crystalline variety. Tin occurs in three allotropic modifications, *viz.* grey tin (diamond-type crystals), white tin (tetragonal crystals) and brittle tin (rhombic crystals) ; lead does not exhibit allotropy. Graphitic carbon and crystalline silicon are good conductors of electricity and show metallic lustre.

Metallic and non-metallic character : With the increase of atomic weight, the electrical properties of the elements gradually change. Thus, carbon is electronegative, silicon is one of the most weakly electronegative elements, but tin and lead are electropositive. This is evidenced by the heats of formation of the oxides and chlorides, which increase from carbon towards silicon. As a result of the development of electropositive character with increasing atomic weights, there is a decrease in the acidic character of the oxides and basic character of hydrides of similar formulae from carbon to lead. In this respect, the B-sub-group of Group IV differs from the B-sub-groups of the earlier groups, in which the electropositive character decreases with increasing atomic weights.

Hydrides : In considering the tetravalent compounds of these elements, we would find that C, Si and Sn form gaseous covalent hydrides (XH_4), carbon and silicon forming other hydrides as well. Formation of PbH_4 is uncertain. Hydrides of carbon are very stable, but the silicon hydrides are unstable (unlike hydrides of carbon, they are decomposed by alkali solutions). Tin only forms SnH_4, which is very unstable and decomposes even at room temperature. Thus, the stability of these hydrides decreases with the increase in atomic weights of the elements.

Halides : All the four elements form tetrachlorides (XCl_4) which are highly volatile covalent compounds (non-ionisable). With the exception of CCl_4, these tetrahalides are hydrolytically decomposed by water. [The hydrolytic stability of CCl_4 is explained on the basis of the *covalency maxima* of 4 for carbon atom, as a result of which it cannot accommodate more than 8 electrons. So, the C-atom in CCl_4 cannot further accomodate an electron-pair from the oxygen atom of a water molecule, and as a result, no hydrolytic decomposition takes place.] In addition to the above chlorides, carbon and silicon from chloroforms of the formula $XHCl_3$, but tin and lead do not form such compounds.

Oxides : All these elements from oxides of the formula XO_2. Carbon dioxide is gaseous and acidic, forming a solution of the weak acid, H_2CO_3, in water. SiO_2 is a crystalline solid and is also weakly acidic. It forms polymeric *giant molecules* in which each silicon atom is bonded by single bonds to four different oxygen atoms. SnO_2 and PbO_2 are stable solids, very weakly acidic, but possessing feeble basic properties as well.

Among the bivalent compounds of these elements, those of tin and lead are most stable. Carbon and silicon form monoxides which are sufficiently different from those of the other elements of this sub-group. Carbon monoxide is a reducing and combustible gas and is neutral in character. It is insoluble and unreactive with water, but is converted to formate on heating with alkalis. It forms addition-compounds with halogens and sulphur and gives rise to metal carbonyls and their derivatives on reacting with certain metals and their compounds. Silicon monoxide is a black, glossy, friable resinous substance, as hard as silicon itself. On being heated, it decomposes into silicon and silica. It forms no salt with acids, but is soluble in HF. The oxides SnO and PbO are distinctly basic solids, but they also show amphoteric properties. Thus, they dissolve in acids to form salts, and also in alkalis to form stannites and plumbites : $SnO+2NaOH=Na_2SnO_2+H_2O$; $PbO+2NaOH=Na_2PbO_2+H_2O$. The hydrated stannates and plumbates of alkali metals, such as $K_2SnO_3, 3H_2O$ and $K_2PbO_3, 3H_2O$ are isomorphous. Bivalent tin compounds are strong reducing agents and easily change into the tetravalent compounds, but bivalent lead compounds are more stable than the tetravalent compunds of the metal. The halogen compounds of bivalent tin and lead, such as $SnCl_2$ and $PbCl_2$, are ionisable salts. Stannous salts are readily hydrolysed in aqueous solution, but the plumbous salts of strong acids are not at all hydrolysed by water.

Carbon is an essential constituent of organic compounds. The other elements of this family also take part in the formation of organo-inorganic compounds such as $Pb(C_2H_5)_4$, $(CH_3)_2\,SiCl_2$ *etc.*

Similarities between boron and silicon : Diagonal relationship.—

As the first member of Group III elements, boron exhibits certain close similarities with the second element, silicon, of the next group (Group IV), and this is generally referred to as the *diagonal relationship* in the Periodic Table (See volume I, p. 125). The similarities are stated below :

(i) Both the elements are high-melting non-metals which are practically non-conductors of electricity. They are insoluble in water and are not affected by dilute acids. But, they evolve hydrogen when fused with alkalis.

(ii) Both boron and silicon exhibit allotropy. Their crystalline and amorphous varieties are known.

(iii) The oxides of both the elements are acidic. They are sparingly soluble in water, and react with bases to form borates and silicates respectively.

(iv) Several covalent hydrides of both the elements are known, and there exist much similarities among the hydrides such as B_2H_6, Si_2H_6 ; B_4H_{10}, Si_4H_{10} *etc.*

(v) The halides of boron and silicon are also covalent compounds and have similar properties. Thus, both boron fluoride (BF_3) and silicon fluoride (SiF_4) are colourless gases which are easily hydrolysed by water : $4BF_3+2H_2O=HBO_2+3HBF_4$; $3SiF_4+3H_2O=H_2SiO_3+2H_2SiF_6$.

(vi) Both boron and silicon are capable of forming larger molecules by chain formation either between their atoms (as in boranes and silanes) or through the mediation of oxygen atoms (as in their oxides and polymeric borates and silicates).

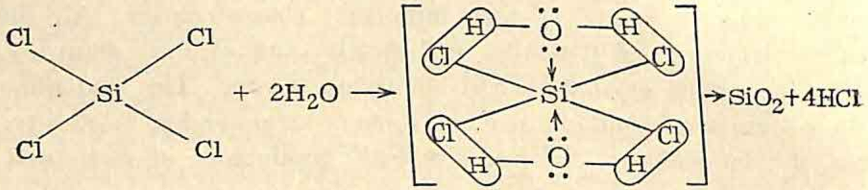
(vii) Both boron and silicon form cationic complexes such as acetylacetonates. (See also volume I, p. 305)

[The conspicuous differences between boron and silicon are their valencies (which is 3 for boron and 4 for silicon) and the reaction with nitrogen at high temperatures, when boron forms a nitride but silicon does not react.]

Comparison among boron, carbon and silicon.

The three elements, boron, carbon and silicon, show very close resemblance in many of their important characteristics. All the three elements are typically non-metals and exhibit allotropy, existing in both crystalline and amorphous forms. The crystalline allotropes have metallic lustre and some of them conduct electricity, but the amorphous varieties are bad conductors of heat and electricity.

The three elements are stable solids with low atomic volumes and densities and very high melting points. They are generally less reactive and do not react with water and dilute acids. [Carbon and silicon, however, decompose steam at high temperatures : $C+H_2O=CO+H_2$; $Si+2H_2O=SiO_2+2H_2$.] Conc. HNO_3 or conc. H_2SO_4 oxidises boron and carbon. But, silicon is not attacked by these acids. A mixture of any one of these acids and hydrofluoric acid, however, attacks silicon to form hydrofluosilicic acid, H_2SiF_6. When fused with alkalis, boron and silicon form borates and silicates respectively, but carbon is not affected by fused alkalis : $2B+2KOH+2H_2O = 2KBO_2+3H_2$; $Si+2NaOH+H_2O = Na_2SiO_3+2H_2$. All the three elements burn and are oxidised when heated with oxygen. The resultant B_2O_3 and SiO_2 are solids, insoluble in water, while CO_2 is a gas, which is somewhat soluble in water, giving unstable H_2CO_3 in solution. All these oxides are acidic. The solutions of alkali metal borates, carbonates and silicates are largely hydrolysed in aqueous solution, so that these solutions react alkaline. Boron and silicon react with halogens at elevated temperatures, forming the corresponding halides. But, the halides of carbon cannot be prepared by the direct union of the two elements ; they are generally prepared by indirect methods. The halides of carbon are not generally hydrolysed, while those of boron and silicon readily hydrolyse to give the corresponding acids : $BCl_3+3H_2O=H_3BO_3+3HCl$; $SiCl_4+2H_2O=SiO_2+4HCl$. [BCl_3 is an electron-deficient compound and in it, the *covalency maxima* of boron atom is not attained. Hence, it can accomodate electrons donated by the oxygen atom of H_2O molecule, and undergo hydrolysis. The *covalency maxima* of silicon is 6 and as such it can attain 12-electron sheath in the outermost shell. $SiCl_4$ is, therefore, hydrolysed by water by accomodating electrons donated by the H_2O molecules.]



Hydrolysis of $SiCl_4$

Many covalent hydrides of these three elements are known. Boron and silicon form only *saturated* compounds with hydrogen, but the hydrocarbons may be *saturated* or *unsaturated*. The capacity of forming chains through bonding of two adjacent atoms of the same element is well-illustrated in these compounds. But, such a capacity is maximum in the case of the carbon atom, and the other two elements (B and Si) exhibit this capacity to a limited extent. Compounds in which one or more hydrogen atoms of these hydrides are replaced by other groups or atoms are also known, *e.g.* $CHCl_3$, $SiHCl_3$, $(C_2H_5)B_2H_5$, $R_3Si(OH)$ *etc.* Cyclic compounds of these three elements are also known, *e.g.* borazole, benzene, certain silicates. Boron and carbon react with nitrogen at high temperatures to form boron nitride and cyanogen respectively ; but silicon does not form a nitride. All the three elements combine with certain metals to form borides, carbides and silicides, such as Mg_3B_2, Mg_2C_3, Al_4C_3, CaC_2, Mg_2Si *etc.*

CARBON

Symbol : C ; *Atomic No.* = 6 ; *Atomic wt.* = 12·00.
Electronic configuration : $1s^2 2s^2 2p^2$.

Occurrence : Naturally occuring carbon has two isotopes, *viz.* ^{12}C (98·89%) and ^{13}C (1·11%). Another isotopic modification, ^{14}C, occurs only in traces, and it is formed in the upper atmosphere by the slow-neutron capture by nitrogen atoms. This variety of carbon is radioactive (β-emitter ; $T_{\frac{1}{2}} = 5570$ years) and it forms the basis of radio-carbon dating (see volume I, p. 216).

Carbon is the main constituent of all living organisms—both plants and animals. Carbon compounds play a vital role in all living processes. Carbon dioxide (CO_2) occurs only in small concentrations (about 0·3 volume percent) in the atmosphere, but its amount from this source far exceeds that available in the vegetable and animal kingdom. Green plants absorb CO_2 from air, and with the help of the green pigment *chlorophyll*, sunlight and water, synthesise carbohydrates, with the elimination of oxygen—a process commonly known as **photosynthesis**. Animals obtain carbohydrates from the plant kingdom. The carbohydrates are degraded to CO_2 through the process of *respiration* of living bodies or by their decay, and the gaseous compound escapes into the atmosphere. The CO_2 thus enters into a continuous cycle between the organic world and the atmosphere.

Metallic carbonates occur in nature as minerals and ores like calcite or limestone ($CaCO_3$), magnesite ($MgCO_3$), dolomite ($CaCO_3 . MgCO_3$), siderite or spathic iron ore ($FeCO_3$), smithsonite ($ZnCO_3$), rhodo-chrosite ($MnCO_3$) *etc*. Petroleum is a mixture of carbon compounds (mainly hydrocarbons). Coal is mostly carbon, admixed with some carbon-compounds. In the elemental state, carbon occurs in nature as diamond and graphite.

Allotropic modifications of Carbon.

Carbon occurs in various allotropic modifications, which can be divided into two categories, *viz*. (i) the crystalline varieties and (ii) the amorphous varieties. The crystalline allotropes of carbon include **diamond** and **graphite**, while the amorphous allotropes are **charcoal (wood charcoal, bone charcoal, blood charcoal), coke, gas-carbon** and **lampblack.** All these materials are nothing but the allotropes of one and the same element, *i.e*. carbon, and this is substantiated by the fact that all of them produce nothing but CO_2 when completely burnt in air or oxygen and, if the same weight of any of the *pure* allotrope is burnt, the amount of CO_2 formed is the same.

It may be mentioned here that, modern investigations, mainly by X-ray analysis, have pointed out that the fine structure of many forms of amorphous carbon is essentially the same as that of some crystalline varieties (such as graphite) and the amorphous nature results only as a consequence of haphazard orientation of the micro-crystalline particles in the mass of the material.

CRYSTALLINE ALLOTROPES OF CARBON.

(i) **Diamond :** Diamond occurs in nature along with fragmented rocks or pebbles at many places in South Africa, Brazil, Mexico, New South Wales, California, Ural mountains, Congo and India (Golconda). Colourless or slightly coloured and transparent diamonds are used as gem-stones, but the dark-coloured or black diamonds (*boarts*) are generally employed in drilling or grinding and cutting work.

Diamond is transparent and lustrous. It is the hardest substance known (the index being 10 in the Moh's scale of hardness ; it is about 150 times harder than corundum), but is brittle. Its density (3·52) is highest of all the allotropic modifications of carbon and it has a refractive index of 2·42. Its heat of combustion is 7·873 Kcals/gm. Diamond does not conduct heat or electricity. It is transparent to X-rays.

Diamond is chemically very inert. It is unaffected by acids and alkalis under ordinary conditions. But, when fused with sodium carbonate, diamond produces sodium oxide and carbon monoxide : $Na_2CO_3+C=Na_2O+2CO$. At about 700° – 800°C, diamond burns in oxygen and fluorine to form CO_2 and CF_4 respectively.

X-ray difraction studies have shown that diamond forms octahedral or cubic crystals. In the diamond crystal, each carbon atom is covalently bound and tetrahedrally surrounded by four other carbon atoms at a distance of 1·54Å. Such a structure is extended throughout each entire crystal in three dimensions and each crystal is, in fact, a *giant molecule* by itself. Extreme hardness and high melting point of diamond is the direct result of such a structure, since rupture of the

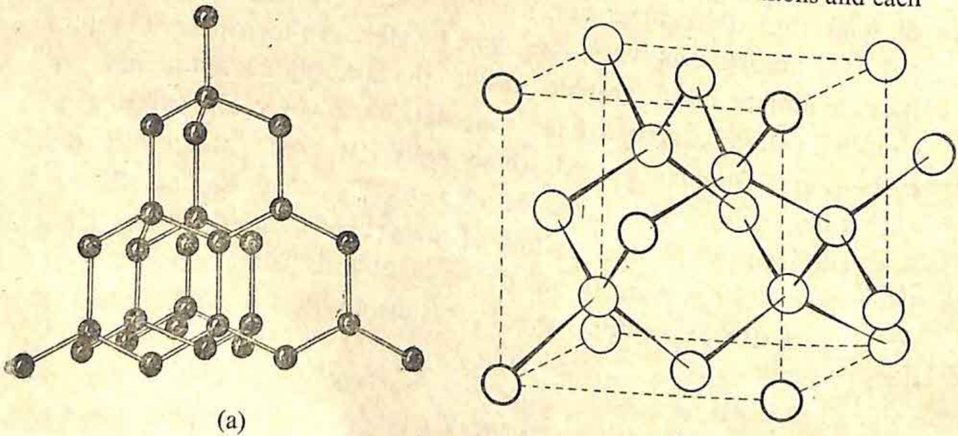

(a) (b)

Fig. 15-1.—Structure of diamond : (a) Schematic, (b) actual.

structure would require the breaking of many covalent bonds. The lack of electrical conductivity of diamond is the obvious consequence of the complete pairing of all the available electrons so that they are firmly held in the C – C bonds.

Artificial or synthetic Diamond—Despite many attempts, preparation of artificial diamond on a commercial scale met with little success. Moissan described (1893) his preparation of small pieces of diamond as follows : a mixture of sugar charcoal and iron powder was heated in an electric furnance at 3000°C and the melt was suddenly chilled. Molten iron dissolved carbon, which separated as small black or colourless crystals of diamond on such cooling. Iron was dissolved out from the solidified melt by HCl to get the crystals of diamond.

Weight of Diamond : The weight of diamonds is expressed in *carats* (1 carat = 0·20 gm.). The largest diamond which has yet been found is the *Cullinan* diamond (3024 carats) ; other well-known diamonds are the *Regent* (193 carats), the Orloff (193 carats), the *Great Mogul* (186 carats), the *Kohinoor* (106 carats), the *Pitt* (136 carats) and the *Hope* (44·5 carats).

(ii) **Graphite :** Graphite (*plumbago* or *black lead*) occurs native in considerable quantities in Sri Lanka (Ceylon), Madagascar, the United States (California), Siberia, New Zealand, Korea, Spain and in the Bohemian mountains. It is a dark grey (almost black) and opaque substance with a density of 2·25. It is soft, greasy to touch and it marks paper. Graphite resembles metals in lustre and in excellent electric and thermal conductivity.

Graphite forms a two-dimensional sheet-like polymeric structure, in which the carbon atoms are arranged in regular hexagons, the C – C bond distance being

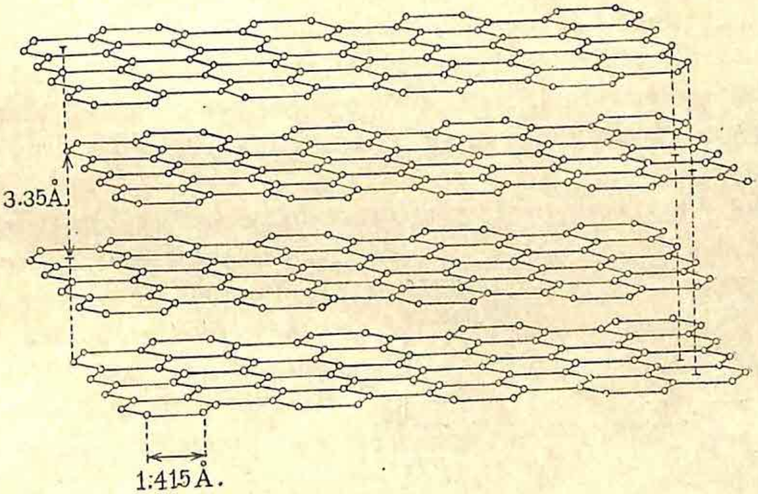


Fig. 15-2.—Structure of graphite

1·415Å. The sheets are placed in layers, one above the other, at a distance of about 3·35Å, and this preculdes the formation of covalent bonds between carbon atoms of two adjacent layers. The layers are held together by comparatively weak Van der Waals force. The overall structure is, therefore, that of a giant molecule. The wide separation of the layers accounts for the lower density of graphite in comparison to diamond. Graphite is quite soft and cleaves easily between the layers which may also slide easily over each other ; hence, it has lubricating properties and greasy feel. In a sense, each layer in a graphite crystal may be regarded as a combination of benzene rings (although it is more quinone-like than aromatic). Only three of the valency electrons of each carbon atom in the graphite crystal are involved in forming sp^2-hybrid bonds, the fourth electron forming a π-bond. As the π-electrons are mobile, graphite can conduct electricity.

Graphite is more easily attacked chemically than is diamond. Its heat of combustion is 7856 cal./gm. It reacts with many atoms, molecules and ions which actually go in between the layers and thus increase the distance between the layers greatly. Thus, graphite forms bronze-coloured compounds with metallic potassium, rubidium or cesium. Cl_2, Br_2, $FeCl_3$, MoO_3, FeS_2 and NH_3 may also penetrate into the graphite structure in this way. When heated at about 700°C and 420°C in an atmosphere of oxygen or fluorine, graphite forms CO_2 or CF_4 respectively. Fusion of graphite with sodium carbonate forms Na_2O and CO, by a reaction similar to that of diamond. Treatment of graphite with strong oxidising agents like HNO_3, perchloric acid or potassium permanganate yields green-to-brown non-conducting and non-stoichiometric oxygenated products known variously as *graphitic acid* or *graphitic oxide*. On heating graphite with a mixture of conc. H_2SO_4 and K_2SO_4, a black product of indefinite composition, often known as *graphon sulphate*, is formed. Complete oxidation of graphite gives *mellitic acid*, a derivative of benzene.

Graphite is used in the preparation of electrodes, crucibles, lead pencils, carbon-arc cores *etc.* It also finds application as a coating for casts in electrotyping, as lubricants in heated machine-parts and as moderator in nuclear reactors.

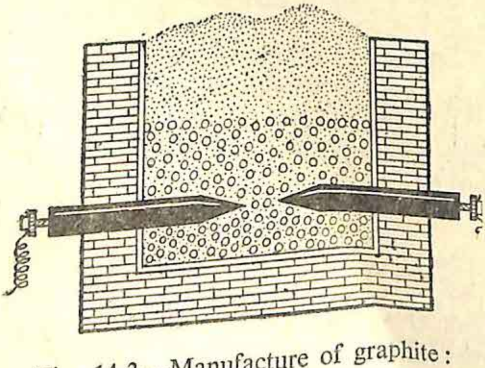


Fig. 14-3.—Manufacture of graphite : Acheson process.

Artificial graphite : Graphite is manufactured artificially from amorphous carbon by the *Acheson process.* A mixture of powdered coke, sand and pitch is taken in an electric furnace (fig.15-3), in which the current is led by two stout carbon electrodes embedded in the mixture. A temperature of about 3000°C is raised, when graphite is formed. It seems probable that, during the heating operation, silicon carbide (SiC) is initially formed and this decomposes at the high temperature into graphite and elemental silicon which vaporises out: $SiO_2+2C=SiC+2CO$; $SiC=Si+C$ (graphitic variety).

AMORPHOUS VARIETIES OF CARBON.

Various forms of carbon, other than diamond and graphite, are included in amorphous carbon. These are mainly impure carbon (except *sugar charcoal*, which is more or less pure carbon). Technically, the most important amorphous carbon are *wood charcoal*, *sugar charcoal*, *animal charcoal* (including *bone charcoal* and *blood charcoal*), *lamp black* (or *soot*), *coke* and *gas-carbon*.

Wood charcoal: Wood charcoal is obtained by heating dried wood in absence of air (destructive distillation of wood). It was earlier carried out in charcoal burners' mounds; but, at present, carbonisation of wood is performed in large iron retorts for the recovery of valuable distillates which contain methyl alcohol, acetic acid, wood tar *etc*.

Sugar charcoal: This is obtained by distilling sugar in absence of air, or by charring sugar by the action of conc. H_2SO_4. The black product obtained is washed with water and then heated with chlorine to remove any residual combined hydrogen. The excess of chlorine is finally removed by heating in hydrogen.

Animal charcoal: Bone charcoal.—Destructive distillation of animal bones produce *bone charcoal*. Pieces of bones are at first treated with super-heated steam to remove fat and marrow. The dried bones are then distilled from retorts in absence of air. The liquid distillate, obtained therefrom, contains aqueous ammoniacal liquid and an oil, called *Dippel's bone oil*, whic hcontains valuable organic bases like pyridine. The residue in the retort contains *bone charcoal* as a black material. Bone charcoal contains about 90% incombustible materials like calcium phosphate and calcium carbonate which is the main constituent of animal bones. These are dissolved out by treating bone charcoal with HCl. The insoluble residue forms deep black powder, known as *ivory black*.

Blood charcoal is obtained by heating dried blood with potash, and leaching the product of calcination.

Properties of Charcoal : A black, porous material, charcoal has a density of 1·4 to 1·9, depending upon the source and mode of its production. Due to inclusion of large amount of air in its pores, the apparent density of charcoal is lowered to about 0·2, and as such, charcoal floats on water. It is not a good conductor of heat and electricity. Chemically, charcoal is much more reactive than diamond and graphite. It burns in air (or oxygen) and fluorine at about 400°C to form CO_2 and CF_4 respectively. With insufficient amount of air or oxygen, carbon monoxide is formed. Powdered charcoal reacts with sulphur vapour at elevated temperatures to form carbon disulphide : $C+2S=CS_2$. It is a good reducing agent, and reduces many metallic oxides (*e.g.* Fe_2O_3, PbO, CuO, ZnO, SnO_2 *etc.*) to the corresponding metals at high temperatures. It also reduces steam and CO_2 at red-heat to hydrogen and carbon monoxide respectively : $Fe_2O_3+3C=2Fe+3CO$; $ZnO+C=Zn+CO$; $H_2O+C=H_2+CO$; $CO_2+C=2CO$. Charcoal is not affected by alkalis, halogens and HCl. But, conc. HNO_3 and H_2SO_4 separately oxidise it to carbon dioxide : $C+2H_2SO_4=CO_2+3SO_2+2H_2O$; $C+4HNO_3=CO_2+4NO_2+2H_2O$. Due to its high porosity, charcoal absorbs many gases and decolorises many coloured solutions.

Uses of Charcoal : Wood charcoal is used as a reducing agent in metallurgy and as a decolorizing and clearifying agent for liquids such as oils, sugar solutions *etc.* As a gas-absorbing agent, it is used in gas-masks (charcoal prepared from dried cocoanut-shell possesses much better absorbing power). It is also used for preparing filter-beds. Charcoal powder is an ingredient of gun-powder. It is often used as fuel for domestic purposes and in goldsmith's shop. Bone charcoal is widely employed for the removal of coloring matters and other impurities from solutions, and especially for the purification of sugar syrups. It is also used as a black pigment (*bone-black*) for shoe-polishes, stencil colours *etc.* Ivory black is used in artists' colours. Blood charcoal or sugar-charcoal is used in medicine for the elimination of certain poisons or of excessive accumulation of gas in the bowel.

Activated charcoal : Charcoal possessing high absorptive powder for gases and high decolorising power for dissolved substances is known as **activated (or active) charcoal.** Such activity of the charcoal depends to a considerable extent, not only on the starting material, but on the way in which it is prepared. Even after the preparation, the activity of a sample of *active charcoal* may often be increased by subsequent special treatment, such as by heating it with certain inorganic salts. Cocoanut-shell, on carbonisation, directly produces active charcoal with excellent absorptive power. From ordinary charcoal, the active variety is generally prepared by briquetting powdered charcoal with wood-tar and a little NaOH and heating the briquettes gradually to 500 – 600°C and ultimately completing the operation by heating in a current of super-heated steam at about 800 – 1000°C. The lost activity of an active charcoal may be recovered by boiling with NaOH solution, filtering and washing the residue with water and drying. Activated charcoal acts as a catalyst in many chemical preparations.

Lampblack or Soot : This form of amorphous carbon is formed by the thermal decomposition of many gaseous or vaporised hydrocarbons. It is manufactured by burning tar, tar oil, napthalene, paraffin oil or natural gases in an insufficient supply of air and chilling the flame on the surface of a water-cooled revolving drum or metal plate. Lampblack has a density of 1·7-1·8 and it does not conduct heat or electricity. It is largely used under the name *carbon black* as a pigment, for the manufacture of printer's ink, drawing inks, artists' colours, for colouring patent leather and rubber-products and also in the vulcanization of rubber.

Gas-carbon : This variety of carbon (also known as *retort carbon*) is obtained as a by-product during high-temperature carbonisation of coal. The gaseous products expelled during carbonisation decompose to certain extent as they sweep over the very hot walls of the retorts and deposit carbon there in the form of a very hard and dense mass.

Gas-carbon is almost pure carbon. It possesses good electrical conductivity and chemical inertness of graphite, but is less dense (density is about 2) than graphite. X-ray analysis shows that gas-carbon has exactly the same crystal structure as true graphite, but the crystallites are of very much smaller size. The hardness of gas-carbon is due to the random arrangement of its crystallites throughout its mass. It is largely used as rods for arc lamps, and as electrodes in galvanic cells.

Coke : This variety of amorphous carbon is impure carbon, and is obtained by strongly heating (coking or carbonizing) coal in absence of air. The impurities in coke are mainly some mineral matters and substances containing nitrogen and sulphur. Coke is a porous substance and a bad conductor of heat and electricity.

Two types of cokes, *viz. gas coke* and *coke-oven coke* are available. Gas coke is obtained by destructive distillation of bituminous coal which are suitable for the manufacture of coal-gas. It is porous and has high ash-content, and is generally used as fuel. Coke-oven coke is obtained in a similar process from *coking coals* which evolve less gas and sinter strongly to form relatively dense and strong coke during distillation. Such coke is used in metallurgical processes.

Coke is widely used as a fuel and a reducing agent in metallurgy.

Coal : A black, carbonaceous mineral, coal is of vegetable origin and is the ultimate product of slow decomposition of the vast primaeval forests submerged under earth in the remote past. Coal was one time regarded as an allotropic modification of carbon. But, the results of the destructive distillation of coal have since proved that it is a complex combination of various substances, in which carbon is associated with other elements like hydrogen, oxygen, small amounts of nitrogen and sulphur, together with compounds of certain other metals and non-metals. The slow decomposition of vegetable matter under earth, in the limited or no supply of air and in presence of high temperature and pressure, is responsible for the formation of coal. In the course of decomposition, some portion of carbon, hydrogen and oxygen is converted into and eliminated as CO_2, H_2O and CH_4. As a result, the residue become increasingly rich in carbon, and the character of the coal changes with time during which the decomposition has taken place. The following varieties of coal are obtained as successive stages of such a process : **Peat, Lignite (or brown coal), Bituminous coal and Anthracite.** (The carbon-content of each variety of coal is : Peat-60% ; Lignite-67% ; Bituminous coal-88·4% ; Anthracite-94%).

Comparison of the different allotropes of Carbon.

Allotropes	Colour and appearance	Hardness and density	Electrical conductivity	Effect of Heat
Diamond	Colourless* and transparent. High refractive index and lustrous. (Crystalline)	Extremely hard. Sp. gr. = 3·5	Bad.	Changes to graphite on strong heating
Graphite	Grey (black) and opaque with metallic lustre. (Crystalline)	Very soft. Sp. gr. = 2·5	Good.	Stable.
Charcoal	Black and opaque (Amorphous)	Soft and porous. Sp. gr. 1·4 – 1·9	Bad.	Changes to graphite.
Lamp black	Black and opaque (Amorphous)	Soft powder. Sp. gr. = 1·8	Bad.	,,
Gas-carbon	Black and opaque (Amorphous)	Very hard. Sp. gr. = 2·0	Bad.	,,

* Dark coloured or black varieties (boarts) are also found.

Coal is industrially a very important material. Apart from its use as a fuel, it is, the source for the manufacture of coal-gas and coal-tar. Coal-tar is, in turn, the source of a host of important aromatic substances. Coal is also used for the manufacture of synthetic petrol.

Coal is largely available in U.S.A., Great Britain, U.S.S.R., Germany and India.

COMPOUNDS OF CARBON

Although carbon mainly forms compounds in only one valence state, *viz*. quadrivalent state, the multiplicity of its compounds is enormous. Compounds of trivalent carbon are rare and of complex nature, found only in the domain of organic chemistry. Similar is the situation with compounds of bivalent carbon, which are highly unstable except carbon monoxide. But, in this compound, carbon in *only formally* bivalent. **Hydrides of carbon or hydrocarbons** are of different types and compositions. But, as they are generally dealt with in Organic Chemistry, we shall not discuss them here.

Oxides of Carbon : The three important oxides of carbon are carbon monoxide (CO), carbon dioxide (CO_2) and carbon suboxide (C_3O_2). They are all gaseous at ordinary temperatures.

Carbon monoxide (CO) : This oxide is formed when carbon is burned with a deficiency of air or oxygen : $2C+O_2=2CO$. Carbon monoxide is generally prepared in the labortory by adding formic acid dropwise to conc. H_2SO_4 heated to about 100°C : $HCOOH=CO\uparrow+H_2O$. The evolved CO may be passed through a solution of NaOH to remove any CO_2 or SO_2 formed, and the pure gas is collected over water (or mercury). Glacial phosphoric acid may be substituted for conc. H_2SO_4 in the preparation.

The gas may also be pepared by heating oxalic acid with conc. H_2SO_4, when CO, CO_2 and H_2O are formed. Carbon dioxide, formed in the preparation, may be removed by passing the gas-mixture through KOH solution : $(COOH)_2=CO_2\uparrow+CO\uparrow+H_2O$.

Alternatively, conc. H_2SO_4 may be allowed to react with potassium cyanide or powdered potassium ferrocyanide to prepare carbon monoxide :

$$2KCN+2H_2SO_4+2H_2O=K_2SO_4+(NH_4)_2SO_4+2CO\uparrow\ ;$$

$$K_4[Fe(CN)_6]+6H_2SO_4+6H_2O$$
$$=2K_2SO_4+FeSO_4+3(NH_4)_2SO_4+6CO\uparrow.$$

Carbon monoxide is obtained as a by-product in the industrial preparation of hydrogen by the partial oxidation of methane [CH_4+H_2O (vapour)$=CO+3H_2$], and in the manufacture of calcium carbide ($CaO+3C=CaC_2+CO$). It is prepared on a large scale by passing CO_2 gas over red-hot carbon and passing the resultant gases through strong KOH solution to remove any CO_2 present : $CO_2+C=2CO$.

Very pure carbon monoxide may be prepared by the thermal decomposition of nickel carbonyl : $Ni(CO)_4 \rightleftharpoons Ni+4CO\uparrow$.

Properties : Carbon monoxide is a colourless, odourless and poisonous gas. It is combustible, but a non-supporter of combustion. It burns in air with a blue flame, producing carbon dioxide. It is slightly soluble in water, but is more soluble in alcohol. The gas is absorbed by acidified (HCl) or ammoniacal cuprous chloride to form white, crystalline addition-compound, $CuCl.CO.2H_2O$. The toxicity of carbon monoxide is the outcome of its combination with *hæmoglobin* of the blood to form *carboxy-hæmoglobin*, as a result of which blood loses its ability to combine with oxygen (in normal oxygen-exchange process) and thus causes death.

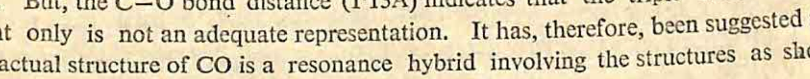
Although carbon monoxide is generally regarded as the anhydride of formic acid, it is practically a neutral oxide. It, however, reacts with NaOH solution at about 160°C and under pressure to form sodium formate : $CO+NaOH=H.COONa$. It similarly reacts with alkali methoxides to form alkali acetates : $CH_3ONa+CO=CH_3.COONa$. When a mixture of CO and steam is passed over calcium oxide at 400°C, calcium carbonate and hydrogen are formed : $CO+H_2O+CaO=CaCO_3+H_2\uparrow$. Strongly heated calcium carbide also absorbs CO to form $CaCO_3$ and carbon : $CaC_2+3CO=CaCO_3+C$. It combines directly with chlorine in presence of sunlight or a catalyst (spongy Pt or animal charcoal) to form carbonyl chloride or phosgene : $CO+Cl_2=COCl_2$. It also unites with sulphur on heating to form carbonyl sulphide or carbon oxysulphide : $CO+S=COS$. A mixture of CO and H_2, when passed over finely divided nickel at about 250°C, forms methane : $CO+3H_2=CH_4+H_2O$. When zinc oxide and finely divided copper are used as catalyst, methyl alcohol is formed : $CO+2H_2O \rightleftharpoons CHO_3H$. (This reaction is often used for the synthesis of methyl alcohol.) Carbon monoxide is a good reducing agent. It reduces many metallic oxides to the corresponding metals at elevated temperatures : $ZnO+CO=Zn+CO_2$; $PbO+CO=Pb+CO_2$; $Fe_2O_3+3CO=2Fe+3CO_2$. Iodine pentoxide is quantitatively reduced by CO at 90°C to elemental iodine : $I_2O_5+5CO=I_2+5CO_2$. Carbon monoxide unites with many metals, and especially with Fe, Co and Ni, when heated with them under pressure, to form *metal carbonyls* : $Ni+4CO=Ni(CO)_4$; $2Co+8CO=Co_2(CO)_8$; $Fe+5CO=Fe(CO)_5$.

Uses : Carbon monoxide is used as a constituent of *water gas* and *producer gas* which are industrial fuels. It is also used for the synthesis of methanol and metal carbonyls and in the extraction of nickel in the Mond's process.

Tests : Carbon monoxide is generally detected and estimated by absorbing in ammoniacal cuprous chloride soln. Small amounts of the gas is detected by shaking it with diluted blood and then treating with tannin soln., when a red ppt. is formed. Even traces of carbon monoxide can be estimated by reacting with I_2O_5 and titrating the liberated iodine with a standard sodium thiosulphate solution, using starch indicator.

Composition and structure of carbon monoxide : The composition and formula of carbon monoxide is ascertained by taking a known volume of the gas with excess of oxygen in an eudiometer tube over mercury. On sparking, carbon monoxide is converted into carbon dioxide and the latter is absorbed by KOH. The results of the experiment show that any volume of carbon monoxide produces its equal volume of carbon dioxide by reacting with half of its volume of oxygen. But, carbon dioxide contains its own volume of oxygen. Hence, carbon monoxide contains half its volume of oxygen. So, 1 vol. carbon monoxide contains $\frac{1}{2}$ vol. oxygen. By applying Avogadro's hypothesis, it comes out that 1 molecule of carbon monoxide contains 1 atom of oxygen ; or, its molecular formula is C_xO (where x is an integer). So, the molecular weight of carbon monoxide is $12x+6$. But, the vapour density of carbon monoxide is 14 and hence, its mol. wt. is 28. Thus, $12x+16=28$; or, $x=1$. So, the formula of carbon monoxide is CO.

The small dipole moment (0·1D) of carbon monoxide and the other properties of the compound are suggestive of the presence of a triple bond in the molecule of CO. But, the C–O bond distance (1·13Å) indicates that the triple bond arrangement only is not an adequate representation. It has, therefore, been suggested that the actual structure of CO is a resonance hybrid involving the structures as shown below, with about equal contribution of each :



$:\overset{+}{C}:\overset{\cdot\cdot\,-}{\underset{\cdot\cdot}{O}}:$ $\quad :C::\overset{\cdot\cdot}{O}: \quad :\overset{-}{C}:::\overset{+}{O}: \quad C\overset{\leftarrow}{\equiv}O$

I II III IV

Metal Carbonyls.

Carbon monoxide acts as a good neutral ligand to form compounds with many metals. These are generally known as '*metal carbonyls*'. The discovery of nickel and iron carbonyls (Mond, 1890)

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and the utilisation of the former in the metallurgy of nickel, opened up a new field in chemistry, characterised by formation of zero-valent-metal compounds. Compounds of the type are formed most commonly by the metals of Periodic Group VIII (except Pd and Pt), less commonly by the transition metals of Group VII A and VI A and still less commonly by certain alkali metals of Group I.

Some important metal carbonyls

Group VI	Group VII	Group VIII
$Cr(CO)_6$	$Mn_2(CO)_{10}$	$Fe(CO)_5$, $Fe_2(CO)_9$, $Fe_3(CO)_{12}$
$Mo(CO)_6$	$Re_2(CO)_{10}$	$Co_2(CO)_8$, $Co_4(CO)_{12}$
$W(CO)_6$		$Ni(CO)_4$

The metal carbonyls are obtained by a variety of procedures, of which the following are important :

(i) Direct synthesis from the finely divided metal and carbon monoxide. Thus, finely divided nickel absorbs carbon monoxide at room temperature and normal pressure to form the tetracarbonyl, $Ni(CO)_4$. Reduced iron powder forms the pentacarbonyl, $Fe(CO)_5$ when heated with CO at 200°C and under 50-200 atmosphere pressure. Cobalt also forms the carbonyl $CO_2(Co)_8$ similarly.

(ii) Indirect synthesis by the action of carbon monoxide on the compounds of the metals in organic solvents during their reaction with Grignand reagents. Thus, the reaction between anhydrous chromic chloride, carbon monoxide and the Grignard reagent produces chromium hexacarbonyl, $Cr(CO)_6$. Similar reactions with molybdenum (v) and tungsten (vi) chlorides produce the corresponding hexacarbonyls.

(iii) The reaction between carbon monoxide and the metal cyclopentadienyls at elevated temperatures also give metal carbonyls.

(iv) Binuclear or dimeric carbonyls of the composition $M_2(CO)_8$ are made by treating a suspension of the metal halide in tetrahydrofuran with carbon monoxide at 200-300 atmosphere pressure and at a temperature of upto 300°C in presence of some powerful reducing agent (*e.g.* Na, Al, Mg *etc.*). $Co_2(CO)_8$ is easily formed by treating $CoCO_3$ with CO and H_2 at 300 atmosphere pressure and 200°C.

$$2CoCO_3+2H_2+8CO=Co_2(CO)_8+2CO_2+2H_2O.$$

The metal carbonyls are covalent compounds and are uniformly diamagnetic. Their covalent characters are indicated by their easy volatility, insolubility in polar solvents and solubility in non-polar solvents. They are decomposed to the metals and CO when heated, although polynuclear carbonyls may sometimes be formed as intermediates. In many reactions, their properties are similar to the metals and carbon monoxide. Thus, nickel tetracarbonyl reacts with bromine to form $NiBr_2$ and CO, whereas with Grignard reagents, its reactions are those of CO. In some of other reactions, the characteristics of the compound are retained, as is shown by the substitution of CO moieties by NO or NH_2 groups. Some metal carbonyls dissolve in alkalis, and the solutions on acidification, form **metal carbonyl hydrides.**

$$Fe(CO)_5 + NaOH \rightarrow Na[HFe(CO)_4] \xrightarrow{H^+} H_2Fe(CO)_4.$$

Many metal carbonyls directly react with halogens to produce **metal carbonyl halides.** Some of the metal carbonyls are highly poisonous. They are generally reducing agents and are easily oxidised by atmospheric oxygen. The carbonyls of Groups VI A metals are more stable and less reactive than the carbonyls of Group VIII metals.

Uses of metal carbonyls : Metal carbonyls are often used to prepare metal powders having spherical granules and for the preparation of pure metal (as n the Mond's process for Ni-extraction). Carbonyls of nickel and chromium are used for making mirrors. Iron pentacarbonyl is used as an anti-knock agent in gasoline.

Structure of metal carbonyls : As the CO moieties in some metal carbonyls can often be substituted successively by neutral molecules, and as one-to-one replacement is effected by molecules like pyridine or ions like CN^-, it is apparent that CO exists as such in a molecule of a metal carbonyl and it occupies the equivalent of one co-ordination position in the structure. The X-ray and electron-diffraction studies of iron carbonyls have indicated that the linkage of CO to the metal is through the carbon atom (and not through the oxygen atom), and this appears to be quite likely due to the enhanced tendency of the carbon atom to become tetracovalent.

In all known metal carbonyls, the metal atom acquires the electronic configuration of the next inert gas. Thus, only the metals of even atomic number in Groups VI to VIII form monomeric carbonyls. The $M(CO)_6$ carbonyls of the Group VI metals form octahedral molecules, that of iron, $Fe(CO)_5$, has trigonal bipyramidal structure ; nickel carbonyl, $Ni(CO)_4$ is tetratedral.

	3d					4s	4p		
$Cr(CO)_6$	↓↑	↓↑	↓↑	↓↑ CO	↓↑ CO	↓↑ CO	↓↑ CO	↓↑ CO	↓↑ CO
$Fe(CO)_5$	↓↑	↓↑	↓↑	↓↑	↓↑ CO	↓↑ CO	↓↑ CO	↓↑ CO	↓↑ CO
$Ni(CO)_4$	↓↑	↓↑	↓↑	↓↑	↓↑	↓↑ CO	↓↑ CO	↓↑ CO	↓↑ CO

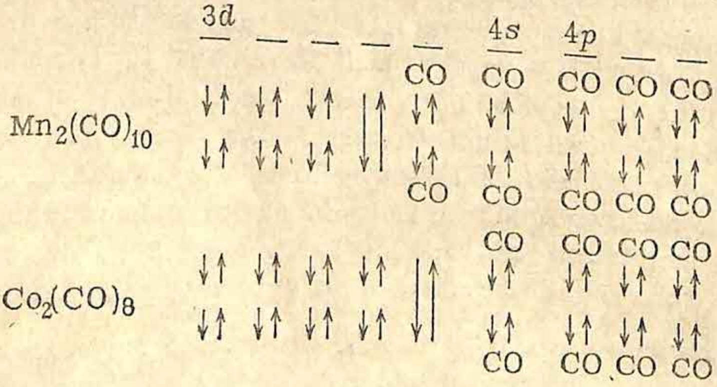
The dipole moment of $Ni(CO)_4$ is zero, indicating that the Ni—C—O bonds are linear ; its electron diffraction studies also supports the linearity. But, the Ni—C bond-distance is much shorter than N—C single bond and the C—O bond distance is intermediate between that of the C—O double and triple bonds.

$$\overset{-}{\text{Ni}} \longleftarrow \text{C} \equiv \text{O} - \quad \longleftrightarrow \quad \text{Ni} \rightleftarrows \text{C} = \text{O} <$$

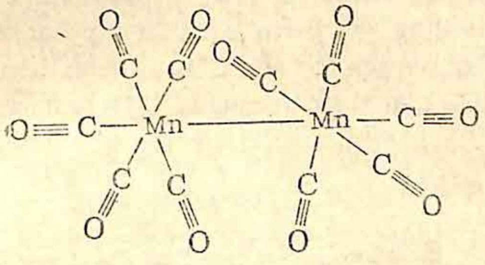
(I) (II)

These results are interpreted as due to considerable contribution to the structure from the doublé-bonded form (II), which is produced by the **'back donation'** of the non-bonding 3*d*-electrons on the nickel atom to the CO molecule (I).

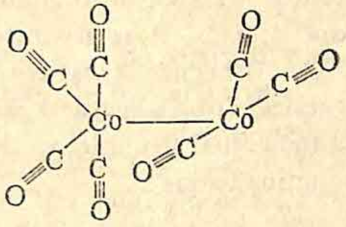
The simplest carbonyls of the elements of odd atomic number are dimeric, *e.g.* $Mn_2(CO)_{10}$, $CO_2(CO)_8$, in accordance with the principle of the attainment of inert-gas structure of the metal atoms.



The dimeric carbonyls of manganese and cobalt have been shown to have the two halves of the molecule linked by direct metal-metal bonds, (III and IV). Bridged structures have also been suggested for them.]



III

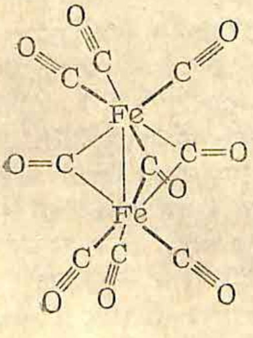


IV

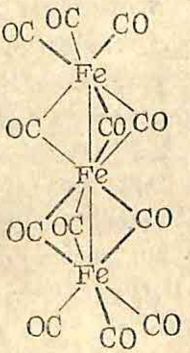
On exposure to light (u.v.) or heat, iron pentacarbonyl loses CO and a yellow, solid, dimeric carbonyl, $Fe_2(CO)_9$ is formed, and this disproportionates above 60°C to a dark green solid carbonyl, $Fe_3(CO)_{12}$ and $Fe(CO)_5$

$$6Fe(CO)_5 \xrightarrow[-3CO]{\text{Light}} 3Fe_2(CO)_9 \xrightarrow{>60^\circ C} Fe_3(CO)_{12}+3Fe(CO)_5.$$

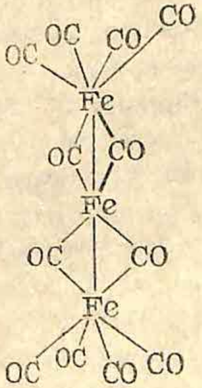
The structure of $Fe_2(CO)_9$, as revealed by X-ray analysis, is as shown in (V), in which the iron atoms are linked by three covalent *ketonic* $>C=0$ bridges. The structure of trimeric tetracarbonyl, $Fe_3(CO)_{12}$, is not exactly known, but the infra-red absorption shows the presence of both ketonic and bridging $>C=0$ groups and terminal carbonyl ($-C\equiv0$) group. Structures VI and/or VII have, therefore been proposed for it.



V



VI



VII

Carbon sub-oxide (C_3O_2) : Very little information is available for carbon suboxide which is the anhydride of malonic acid and is obtained by dehydrating malonic acid with P_2O_5 in vacuum at about 150°C. It is a foul-smelling gas with a boiling point of -7°C. It burns explosively with oxygen to form CO_2. It has been suggested from structural studies that the molecule of C_3O_2 is linear and the actual structure is the resonance hybrid of the following resonating forms :

$$O{=}C{=}C{=}C{=}O \longleftrightarrow \overset{+}{O}{\equiv}C{-}C{\equiv}C{-}\bar{O} \longleftrightarrow \bar{O}{-}C{\equiv}C{-}C{\equiv}\overset{+}{O}$$

Carbon dioxide (CO_2).

Carbon dioxide occurs in the atmosphere to the extent of about 3% by volume. The sources of atmospheric carbon dioxide are mainly the burning of carbonaceous fuels, the respiration of animals, the decomposition of organic matter and the fermentation of sugar. Despite its occurrence in very small amounts in the total atmosphere, carbon dioxide plays a vital role in the synthesis of carbohydrate by the plants (photosynthesis) for their sustenance and growth and also for human consumption. Carbon dioxide also occurs in the water of many springs and it is ejected in enormous quantities at many places from inside the earth through fissures in the earth's crust. In the combined state, it occurs in nature as carbonate minerals such as limestone, chalk, marble, magnesite, dolomite *etc*.

Preparation : Carbon dioxide is formed (i) by the combustion of carbonaceous matter in excess of air or oxygen, (ii) by the thermal decomposition of metal carbonates or bicarbonates (except the carbonates of the alkali metals and barium) or (iii) by the action of dilute acid on metal carbonates or bicarbonates.

In the laboratory, carbon dioxide is commonly prepared by the action of dilute HCl on calcium carbonate (marble chips). [Dil. H_2SO_4 is not used in this preparation, as $CaSO_4$, a product of the reaction, forms an insoluble coating on the pieces of marble and stops further reaction.] The gas is passed through sodium bicarbonate solution, dried by conc. H_2SO_4 and collected over mercury (or by the upward displacement of air, as the gas is much heavier than air).

Pure CO_2 can alternatively and easily be prepared by heating pure sodium bicarbonate or by the acidic decomposition of pure sodium carbonate: $2NaHCO_3=Na_2CO_3+CO_2+H_2O$; $Na_2CO_3+H_2SO_4=Na_2SO_4+H_2O+CO_2$.

Industrially, carbon dioxide is prepared by the thermal decomposition of limestone in a lime kiln (see 'the manufacture of lime' in chapter XIII). The gaseous products formed in the process are passed through a concentrated solution of K_2CO_3, when CO_2 is completely absorbed to from $KHCO_3$. The solution of $KHCO_3$ is decomposed by boiling to obtain carbon dioxide : $K_2CO_3+H_2O+CO_2 \rightleftharpoons 2KHCO_3$. The gas is dried by passing through conc. H_2SO_4.

Large amounts of carbon dioxide is also obtained as a by-product during the production of alcohol by the fermentation of sugar : $C_6H_{12}O_6$ (glucose)$=2C_2H_5OH+2CO_2$. It may also be obtained on a large scale from *water-gas* by catalytic process :

$$\underbrace{CO+H_2}+H_2O \xrightarrow{\text{catalyst}} CO_2\uparrow+2H_2\uparrow.$$

Properties : Carbon dioxide is a colourless, odourless gas with a faintly acid taste. It is about 1·5 times heavier than air. It is non-combustible and non-supporter of combustion. But, ignited sodium, potassium and magnesium metals continue to burn in it with the deposition of carbon : $4Na+3CO_2=2Na_2CO_3+C$; $2Mg+CO_2=2MgO+C$. The gas is not poisonous, but animals cannot breathe in the gas and die in suffocation. Carbon dioxide is fairly soluble in water and forms the unstable, weak carbonic acid (H_2CO_3) in solution ; but, the dissolved gas is expelled on boiling the solution. $H_2O+CO_2 \rightleftharpoons H_2CO_3$. [The aerated waters like *soda-water*, *lemonade* *etc.* contains CO_2 dissolved in water under pressure.] When passed over red-hot carbon (or zinc or iron), carbon dioxide is reduced to carbon monoxide : $CO_2+C=2CO$; $CO_2+Fe=CO+FeO$. [The gas also decomposes into carbon monoxide and oxygen at very high temperatures.]

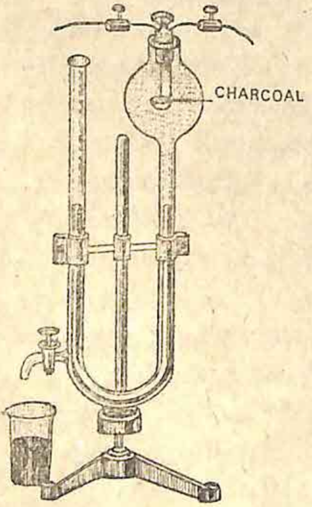
Carbon dioxide is an acidic oxide. It reacts with bases to form carbonates : $Na_2O+CO_2=Na_2CO_3$; $CaO+CO_2 \rightleftharpoons CaCO_3$. When passed through a solution of sodium hydroxide, CO_2 first forms Na_2CO_3 which generally remains in solution. If the passage of CO_2 through this solution is continued, sodium bicarbonate is formed which, being less soluble in water, is often precipitated :

$2NaOH+CO_2=Na_2CO_3+H_2O$; $Na_2CO_3+H_2O+CO_2=2NaHCO_3$. When CO_2 is passed through a clear solution of lime water, the latter turns milky due to the formation of insoluble calcium carbonate. If the passage of CO_2 gas through the *milky solution* is continued, the milkiness disappears due to the formation of calcium bicarbonate which is soluble in water. The resultant clear solution again turns milky on boiling, and this is due to the decomposition of calcium bibarbonate by heat, when calcium carbonate is formed: $Ca(OH)_2+CO_2=CaCO_3\downarrow+H_2O$; $CaCO_3+H_2O+CO_2\rightleftharpoons Ca(HCO_3)_2$.

Dry ice or solid carbon dioxide : Gaseous CO_2 can be liquefied when subjected to a pressure of about 60 atmospheres at ordinary temperature. The liquid is partially evaporated in evaporators, whereby the temperature drops to about 0°C and the pressure to about 30 atmospheres. Under these conditions, the liquid CO_2 is transformed into solid in the form of fine particles of snow, which are pressed into solid blocks of suitable size. The vaporised liquid CO_2 from the evaporators is re-cycled along with fresh quantities of the gas. Solid carbon dioxide or *dry ice* as it is called, is largely used in refrigeration work. In admixture with ether, it produces a temperature as low as −100°C, and it thus helps scientific studies at low temperatures. The greatest advantage of its use is the cleanliness, as the solid directly passes into gas on raising the temperature without going through the liquid stage.

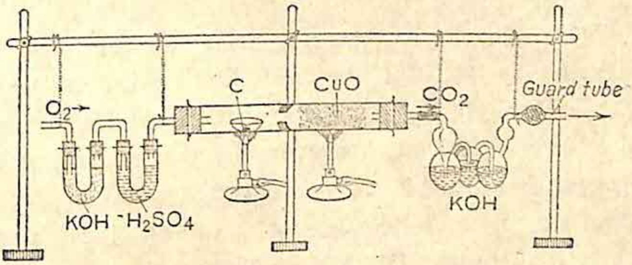
Uses ; Carbon dioxide is used for preparing aerated waters. It is also used to extinguish fire and as a refrigerant in the solid form (*dry ice*). CO_2 is used as an ingredient in the manufacture of sodium carbonate (Solvay Process), urea, salicylic acid *etc*.

Composition and formula of carbon dioxide :



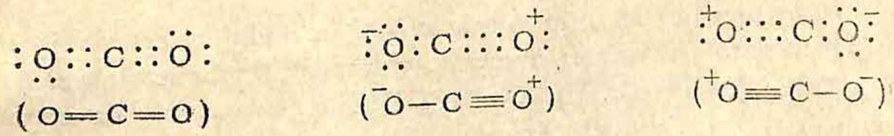
Volumetric composition.—The volumetric composition of CO_2 can be ascertained by electrically burning a small piece of carbon in the globe of the eudiometer tube as shown in the figure in the margin. The globe is previously filled with pure oxygen at atmospheric pressure. [This is done by adjusting the same mercury levels at the two limbs of the tube.] After complete combustion of the piece of carbon and on cooling the apparatus, no change in the mercury levels at the two limbs is observed. This indicates that, no change in volume takes place when O_2 is converted to CO_2. Thus, it is proved that **CO_2 contains its own volume of oxygen.**

Gravimetric composition.—The composition by weight of CO_2 is determined by burning a known weight of pure charcoal in a combustion tube (as shown in the figure below) in a current of dry and pure oxygen, and absorbing the CO_2 formed in an assembly of absorption bulbs containing stroning KOH soln. The potash-bulbs are weighed accurately before and after the combustion to obtain the weight of CO_2 formed. [The use of CuO inside the combustion tube ensures conversion of any carbon monoxide formed into CO_2 and the attachment of soda-lime tube at the end of the potash-bulbs eliminates incoming of any atmospheric moisture and CO_2.]



The results of the experiments slow that the percentages of carbon and oxygen in the CO_2 formed are 27·27 and 72·73 respectively. So, the ratio of the number of atoms of carbon and oxygen in a molecule of CO_2 comes out as $\frac{27{\cdot}27}{12} : \frac{72{\cdot}73}{16} = 1 : 2$. Thus, the empirical formula of CO_2 is $(CO_2)_x$, where x is an integer. Now, the vapour density of CO_2 is 22 and hence, its molecular weight is 44. Thus, $(CO_2)_x = 44$; or $x = 1$. So, the molecular formula of carbon dioxide is $\mathbf{CO_2}$. The formula of CO_2 can also be deduced by applying Avogadro's hypothesis to the data obtained in determining the volumetric composition of the gas.]

The dipole moment of CO_2 is zero. Hence, the arrangement of the atoms in its molecule should be linear. The C – O bond-distance (1·15Å) in CO_2 suggests that the molecule of CO_2 is a resonance hybrid of the following three forms, each one of them making approximately the same contribution :



$:\underset{\cdot\cdot}{O}::C::\overset{\cdot\cdot}{O}:$ $(O{=}C{=}O)$

$\overset{-}{:}\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:C:::\overset{+}{O}:$ $(^{-}O{-}C{\equiv}O^{+})$

$\overset{+}{:}O:::C:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}\overset{-}{:}$ $(^{+}O{\equiv}C{-}O^{-})$

Detection and Estimation of CO_2 : Carbon dioxide is an odourless gas and turns lime water milky. It is estimated by absorbing in a known volume of standard baryta soln., filtering off the precipitated $BaCO_3$ and titrating the excess baryta with a standard acid soln. (using phenolphthalein indicator).

Carbonic acid and Carbonates.

Carbon dioxide is the anydride of the importannt acid, carbonic acid (H_2CO_3), which is formed in solution when CO_2 dissolves in water. The acid is very weak and highly unstable, and in fact, it has not been possible to isolate it in the pure state. [It has, however, been found that, when HCl is added to a suspension of $NaHCO_3$ in anhydrous ether at $-30°C$, the anhydrous acid, H_2CO_3, exists as a stable entity in ether solution, and a solid etherate, $H_2CO_3 \cdot (C_2H_5)_2O$, is precipitated at $-78°C$ as white crystals which decompose above $-10°C$.] Taking for granted that all the CO_2 dissolved in water remains as H_2CO_3, its acid dissociation constants are given as : $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$, $K_1 = 4{\cdot}16 \times 10^{-7}$ and $HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$, $K_2 = 4{\cdot}84 \times 10^{-11}$. [In fact, however, the greater part of the dissolved CO_2 is present in solution as loosely hydrated species.] Carbonic acid, therefore, is a weak dibasic acid and gives rise to two series of salts, *viz*. bicarbonates and carbonates :

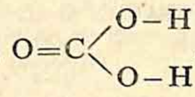
$$NaOH + H_2CO_3 \begin{array}{l} \nearrow NaHCO_3 \text{ (acid salt, bicarbonate)} \\ \searrow Na_2CO_3 \text{ (normal salt, carbonate)} \end{array}$$

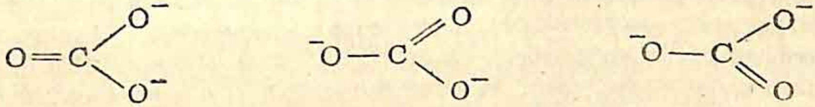
Both normal and bicarbonates of the alkali metals are known in the pure solid state. The bicarbonates of alkaline earth and some other heavy metals exist only in solution, and they decompose into normal carbonates and CO_2 on heating the solutions. The normal conbonates of the alkali metals and ammonium carbonate are soluble in water, but most of the normal canbonates of the heavy metals are practically insoluble in water. Due to the weakly acidic nature of carbonic acid, the solutions of the alkali metal carbonates in water react alkaline because of hydrolysis :

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-.$$

When precipitated from solutions by the addition of solutions of alkali metal carbonates, many heavy metals form basic carbonates [*e.g.* $PbCO_3$, $Pb(OH)_2$, $MgCO_3$, $Mg(OH)_2$ etc.] due to the extensive hydrolysis of the carbonate ion. The alkali metal carbonates can be titrated by strong acids (*e.g.* HCl) in two stages. The use of phenolphthalein indicator during the titration indicates the completion of the first stage of neutralisation, *i.e.* upto the bicarbonate stage, and methyl orange indicator indicates the end-point of complete neutralisation :

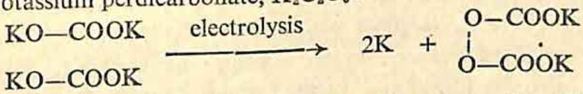
$$Na_2CO_3 + HCl = NaHCO_3 + NaCl \text{ [phenolphthalein, pH} = 8{\cdot}7]$$
$$Na_2CO_3 + 2HCl = 2NaCl + CO_2 + H_2O \text{ [methyl orange, pH} = 4{\cdot}0]$$

Carbonic acid is represented by the structure,  $O{=}C(O{-}H)_2$. The conbonate ion involves sp^2-hybridised carbon atom and has, therefore plane triangular shape (*cf.* Chapter III). X-ray analysis indicates that the three C–O bonds in the carbonate ion are identical. Hence, it is suggested that the structure of carbon ion is a resonance hybrid of the following forms, each making almost equal contribution to the actual structure :



Percarbonates : Metal carbonates containing larger proportions of oxygen in their molecules than that present in a molecule of normal carbonate (such as Na_2CO_3) are commonly known as *percarbonates.* Two types of percarbonates are known, *viz.* **permonocarbonates** and **perdicarbonates,** although their parent acid (permonocarbonic acid and perdicarbonic acid) have not been isolated.

Perdicarbonates : When a saturated solution of potassium carbonate is electrolysed at a low temperature (–15° to –10°C) with platinum electrodes, using high current-density, a pale blue deposit is obtained at the anode. The deposit is washed quickly and successively with cold water, alcohol and ether and dried. The product is potassium perdicarbonate, $K_2C_2O_6$:

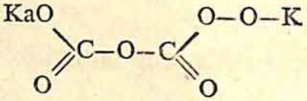


$$\begin{matrix} KO{-}COOK \\ KO{-}COOK \end{matrix} \xrightarrow{\text{electrolysis}} 2K + \begin{matrix} O{-}COOK \\ | \\ O{-}COOK \end{matrix}$$

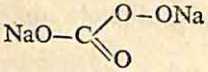
The corresponding sodium salt is prepared analogously. These salts readily decompose into K_2CO_3, CO_2 and O_2 on slight heating, and they readily liberate iodine from neutral KI solution : $2K_2C_2O_6 = 2K_2CO_3 + 2CO_2 + O_2$; $K_2C_2O_6 + 2KI = 2K_2CO_3 + I_2$. It also reduces acidified $KMnO_4$ solution : $5C_2O_6^{2-} + 2MnO_4^- + 16H^+ = 2Mn^{+2} + 10CO_2 + 5O_2 + 8H_2O$.

This type of perdicarbonates are often designated as '*electrolytic perdicarbonate*' to differentiate them from the isomeric compounds obtained by passing a stream of CO_2 gas through an ice-cold solution of alkali peroxide : $Na_2O_2 + 2CO_2 = Na_2C_2O_6$. The corresponding potassium salts are similarly prepared. The two types of perdicarbonates, *viz.* the one prepared electrolytically and the other prepared by chemical methods, differ considerably in their properties, which is accounted for by their different structures. Thus, the amount of iodine liberated by the *electrolytic* perdicarbonate is double that liberated by the other type ; the *electrolytic* perdicarbonate liberate I_2 from KI solution immediately, but the other type liberates I_2 followed by O_2. The *electrolytic* perdicarbonate is supposed to contain *internal* peroxo-group (–O–O–) in the molecule, while the other type of perdicarbonates, *external* (or *terminal*) peroxo-groups in their molecules.

KOOC—O—O—COOK
Electrolytic perdicarbonate
($K_2C_2O_6$)



Synthetic perdicarbonate
($K_2C_2O_6$)

Perexomonocarbonates like Na_2CO_4, $BaCO_4$ *etc.* are prepared by passing CO_2 gas through ice-cold solution or suspension of Na_2O_2 or BaO_2 respectively ; $Na_2O_2+CO_2=Na_2CO_4$; $BaO_2+CO_2=BaCO_4$. Their chemical behaviour suggests the structure, 

Carbonate-perhydrates : When H_2O_2 solution is added to an ice-cold solution of sodium carbonate, and alcohol is added to the reaction-mixture, a white crystalline precipitate of the composition, $Na_2CO_3H_2O_2.\frac{1}{2}H_2O$ is obtained. This is called sodium carbonate-perhydrate. A similar perhydrate has the composition $2Na_2CO_3.3H_2O_2$. These compounds liberate iodine from KI solution very slowly. They are often used in detergent powders.

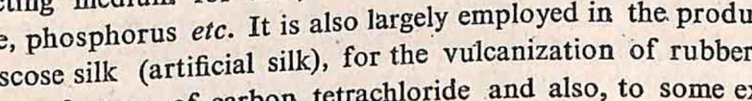
Sulphides of carbon : The principal and important sulphide of carbon is carbon disulphide (CS_2), although other very unstable lower sulphides such as CS and C_2S_3 have been reported in literature.

Carbon disulphide is technically prepared by passing sulphur vapour over white-hot wood charcoal or coke : $C+2S=CS_2$. The reaction is endothermic.

In actual practice, a tall electrothermal furnace, fitted with two stout carbon rod electrodes near the bottom, is filled with powdered charcoal or coke. Sulphur is admitted at the base of the furnace through openings at the side. Powdered coke or charcoal can also be introduced in the furnace through separate openings near the bottom. On striking an arc between the electrodes, the charge in the furnace is heated white-hot and sulphur is simultaneously vaporised. The sulphur vapour ascends and comes in contact with white-hot coke (or charcoal) when CS_2 is formed. Carbon disulphide vapours escape through an exit tube near the top of the furnace and are then condensed into the liquid on passing through water-cooled condenser. The crude CS_2 is purified by shaking with metallic mercury and then re-distilling.

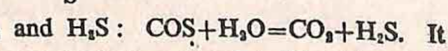
Carbon disulphide is a colourless, volatile and highly refractive liquid, having a density of 1·262 (at 20°C). The pure compound has a faint pleasant odour, but it generally possesses an offensive smell because of the presence of impurities. It boils at 46°C and freezes at −111·6°C. It is almost immiscible with water, but is completely miscible with alcohol, ether and chloroform. It is poisonous. The compound is highly inflammable and its vapours form explosive mixtures with oxygen, air and even nitrogen dioxide. It decomposes water vapour above 150°C : $CS_2+2H_2O=CO_2+2H_2S$. Strong oxidants, such as permanganate, decomposes CS_2 with the deposition of sulphur. It reacts with sulphur trioxide to form carbonyl sulphide (COS, also called carbon oxysulphide) : $CS_2+3SO_3=COS+4SO_2$. When chlorine gas is passed through boiling CS_2 in the presence of small amount of iodine (as catalyst), carbon tetrachloride and sulphur monochloride are formed : $CS_2+3Cl_2=CCl_4+S_2Cl_2$. [In fact, CCl_4 is generally prepared through this reaction. The two products, *viz*. CCl_4 and S_2Cl_2 are separated by fractional distillation.] It reacts with hydrogen at elevated temperatures in presence of Pt-catalyst to form methane and hydrogen sulphide : $CS_2+4H_2=CH_4+2H_2S$. Carbon disulphide reacts with caustic soda solution to give sodium carbonate and sodium thiocarbonate : $3CS_2+6NaOH=Na_2CO_3+2Na_2CS_3+3H_2O$. It also reacts with alkali sulphide solutions to form alkali thiocarbonates : $CS_2+K_2S=K_2CS_3$. It is an excellent solvent for many substances.

The eletron diffraction data on carbon disulphide show that its molecule is linear with C – S bond distance of 1·54A. Such a bond distance can be explained by taking into consideration the following three resonance structures of the molecule, with equal contributions by each :

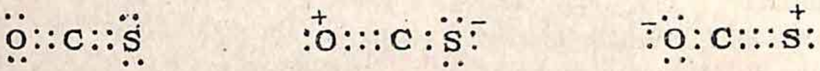


$$\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}::C::\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}} \longleftrightarrow :\overset{+}{S}:::C:\overset{\cdot\cdot -}{\underset{\cdot\cdot}{S}}: \longleftrightarrow :\overset{-\cdot\cdot}{\underset{\cdot\cdot}{S}}:C:::\overset{+}{S}:$$

Carbon disulphide is widely used in industry as a solvent and extracting medium for fats, oils, waxes, resins, rubber, sulphur, iodine, phosphorus *etc.* It is also largely employed in the production of viscose silk (artificial silk), for the vulcanization of rubber, for the manufacture of carbon tetrachloride and also, to some extent, as an insecticide.

Carbonyl sulphide (COS) is a colourless, odourless and inflammable gas which is formed on passing a mixture of carbon monoxide and sulphur vapour through a red-hot tube : $CO+S=COS$. [It is best obtained in the pure state by the action of acids on ammonium thiocarbamate :  $H_2N\underset{\underset{S}{\|}}{C}-ONH_4+2HCl=2NH_4Cl+COS$.] It is slowly decomposed by water into CO_2 and H_2S : $COS+H_2O=CO_2+H_2S$. It reacts with an alcoholic solution of ammonia to form ammonium thiocarbamate :

$COS+2NH_3=H_4N.S.CONH_2$. [Ammonium thiocarbamate forms urea on gentle heating : $H_4N.S.CONH_2=CO(NH_2)_2+H_2S$.]



Structure of carbonyl sulphide

Halides of carbon : Carbon forms a large number of halides which are generally dealt with as the subject-matter of organic chemistry. In the present discussion, we shall mention only a few of them.

Carbon tetrafluoride (CF_4) is formed as a colourless gas (b.p. −128°C) on burning carbon in an atmosphere of fluorine, or by the action of silver fluoride on carbon tetrachloride at 300°C. It is sparingly soluble in water and is extremely stable towards heat. The compound is also unaffected by acids and alkalis. .

Carbon tetrachloride (CCl_4) : It is prepared through the reaction of Cl_2 gas and CS_2 in presence of some halogen-carrier like iodine or $MnCl_2$: $CS_2+3Cl_2=CCl_4+S_2Cl_2$. The resultant S_2Cl_2 is made to react with CS_2 at 60° and in presence of a suitable catalyst (FeS) to produce more CCl_4 and deposit sulphur : $2S_2Cl_2+CS_2=CCl_4+6S$. [The deposited sulphur may be used to prepare CS_2, and the manufacture of CCl_4 thus continues as a cyclic process.] CCl_4, obtained is the above process, is washed with KOH solution, dried and fractionally distilled to get the pure product.

Carbon tetrachloride is a colourless, non-inflammable and highly refractive liquid, with a characteristic smell and narcotic action. It boils at 76·6 C and has a density of 1·5. At ordinary temperatures, it is chemically inert and is unaffected by water, acids or bases. It, however, slowly corrodes metals like Fe and are gradually decomposed by water in presence of these metals, according to the equation, $CCl_4+2H_2O=CO_2+4HCl$. Heated sodium reacts violently with carbon tetrachloride. It is immiscible with water, but is completely miscible with alcohol and other organic solvents.

Carbon tetrachloride forms many important substituted products which are discussed later. It is widely used as an industrial solvent for fats, oils, resins *etc*. It is also used as a fire-extinguishing material and also in medicine.

Carbon tetrabromide (CBr_4) and carbon tetraiodide (CI_4) are solids, melting at 94°C and 171°C respectively, and are formed on heating CCl_4 with $AlBr_3$ and AlI_3 (or BiI_3) respectively.

Carbonyl chloride or Phosgene ($COCl_2$) is a highly poisonous suffocating and colourless gas with a pungent smell. It is formed when a mixture of equal volumes of CO and Cl_2 is exposed to strong sunlight, or is passed over active charcoal : $CO+Cl_2=COCl_2$. Carbonyl chloride may be prepared in the laboratory by adding fuming sulphuric acid dropwise to boiling carbon tetrachloride :

$CCl_4+2SO_3=COCl_2+S_2O_5Cl_2$ (Disulphuryl chloride).

[When chloroform is exposed to air and sunlight, it is oxidised to phosgene : $2CHCl_3+O_2=2COCl_2+2HCl$. Hence, chloroform is generally stored tightly closed in coloured bottles.]

Carbonyl chloride is unstable towards heat, and it completely decomposes into CO and Cl_2 at about 800°C : $COCl_2 \rightleftharpoons CO+Cl_2$. It slowly reacts with water to produce CO_2 and HCl. With ammonia, it forms urea. It is, therefore, regarded as the acid chloride of carbonic acid : $COCl_2+H_2O=CO_2+2HCl$; $COCl_2+4NH_3=CO(NH_2)_2+2NH_4Cl$. It reacts with ethyl alcohol to form diethyl carbonate : $COCl_2+2C_2H_5OH=CO(OC_2H_5)_2+2HCl$.

Carbonyl fluoride (COF_2) and carbonyl bromide ($COBr_2$) are also known.

Mixed halides of carbon : Freons.—Chlorofluoro-derivatives of methane and ethane are known as **freons.** These are prepared by the action of hydrofluoric acid or a metal fluoride (such as SbF_3) on CCl_4, $CHCl_3$ or C_2Cl_6 in presence of a catalyst like $SbCl_5$ (*Swart's reaction*) : $3CCl_4+2SbF_3=3CF_2Cl_2+2SbCl_3$. [Some other chlorofluorocarbons like CCl_3F, $CClF_3$ and carbon tetrafluoride are also produced in the above reaction. The mixture of the above gases are commercially called *freons*. Of these, CF_2Cl_2 is named Freon-12.] Freons are colourless, inert, non-inflammable and non-toxic. They have very low boiling points and can be easily liquefied under pressure. The resultant liquid, on evaporation, absorbs a large amount of heat. Freons are widely used as refrigerants, aerosol bomb propellants and heat-transfer agents.

Teflon or polytetrafluoroethylene (a polymer of tetrafluoroethylene) is a plastic-like material obtained through polymerisation of tetrafluoroethylene in presence of some catalyst. [Tetrafluoroethylene (C_2F_4) is prepared by the action of SbF_3 and HF on choroform and then heating at 800°C the chloro-difluoromethane so produced :

$$CHCl_3 + SbF_3(HF) \rightarrow CHF_2Cl \xrightarrow{800^\circ C} C_2F_4 + 2HCl + \text{other products.]}$$

Teflon, though difficult to work, is a good electrical insulator and is resistant to hot, concentrated acids and alkalis (even to boiling aqua regia).

Hydrocyanic acid and Cyanides : Hydrocyanic acid (HCN) or *prussic acid*, as it is sometimes called, occurs in the combined state in the plant kingdom (*e.g.* as the glucoside *amygdalin* in bitter almonds) and also in small amounts in the free state in crude coal-gas. It is prepared by distilling potassium cyanide with dil. H_2SO_4, drying the evolved gas by fused calcium chloride and condensing it to a liquid by cooling in a freezing mixture : $KCN + H_2SO_4 = KHSO_4 + HCN$. Distillation of powdered potassium ferrocyanide with dil. H_2SO_4 also produces the acid : $2K_4[Fe(CN)_6] + 3H_2SO_4 = 3K_2SO_4 + K_2Fe[Fe(CN)_6] + 6HCN$. Pure HCN may be prepared by passing pure and dry H_2S through mercuric cyanide : $Hg\ (CN)_2 + H_2S = HgS + 2HCN$.

Hydrocyanic acid is a colourless, mobile liquid (b.p.=26·5°C ; density=0·697). It is extraordinarily poisonous and has a distinctive smell. (As little as 50 mg. is sufficient to kill a man within a few seconds. The antidotes for HCN-poisoning are hydrogen peroxide or ferrous hydroxide.) The high dielectric constant (~116) and boiling point of hydrocyanic acid are due to extensive hydrogen-bonding among its polar molecules. The compound is covalent, but it is capable of dissociation in aqueous solution. It is completely miscible with water, alcohol and ether. In aqueous soltion, HCN behaves as a very weak acid ($K_a = 2{\cdot}1 \times 10^{-9}$), and as such, the water-soluble metal cyanides are easily hydrolysed in water, making the solutions alkaline : $CN^- + H_2O \rightleftharpoons HCN + OH^-$ (see vol I, pp. 220-223. Liquid HCN is unstable and polymerises readily.

Hydrocyanic acid is often thought of as existing in two tautomeric forms as shown below, corresponding to nitriles and isonitriles :

$$\mathrm{H:C:::N \rightleftharpoons H:\ddot{N}::C:}\ \text{or,}\ \mathrm{H-C \equiv N \rightleftharpoons H-N=C}$$

But, all atempts to effect their separation have been unsuccessful and as such, the existence of the two forms is doubtful.

Hydrocyanic acid has been used as a non-aqueous ionising solvent.

Metallic cyanides : These are metal-salts of hydrocyanic acid and they can be classified as (i) *the ionic cyanides*, (ii) *the covalent cyanides* and (iii) *the complex cyanides*.

[The cyanide ion, CN^-, is found in the ionic cyanides of the alkali metals. But, the CN group may be attached by a covalent bond either from the carbon or from the nitrogen atom as, $-C{\equiv}N:$, or $:C{\equiv}N-$, and in this way, the organic cyanides and isocyanides (*i.e.*, nitriles and isonitriles) arise. There is the further possibility of the CN group being attached at both ends by covalent bonds, *i.e.* as a bridging CN group, $-C{\equiv}N-$.]

(i) *The ionic cyanides* are formed by the alkali metals (except Li) and monovalent thallium and possibly also by the alkaline earth metals. The formation of such cyanides in the cases of many heavier metals appears to be debarred by the extensive hydrolysis of strongly basic cyanide ion, resulting in the formation of the hydrated oxides or hydroxides of the metals. In these cyanides (M^+CN^-), the C−N bond has been calculated to be about 57% ionic and it is supposed to involve the two resonance forms

$$:\mathrm{C}:::\mathrm{N}: \text{ and } \quad :\overset{+}{\mathrm{C}}::\overset{\cdot\cdot\,-}{\mathrm{N}}:$$

Two important compounds of this category, *viz*. sodium cyanide and potassium cyanide, have been discussed in details under **Sodium** and **Potassium** in Chapter XI.

(ii) Of the *covalent cyanides* (metallic), silver cyanide (AgCN) has been studied in details. Its preparation and certain reactions have been described earlier (see, **'Compounds of silver'**, chapter XII). X-ray studies have shown that in the crystal of AgCN, there are infinite chains of alternate Ag atoms and CN groups, so that the cyanide group is attached at both ends to metal atoms as $-Ag-C{\equiv}N-Ag-$. These chains are arranged in parallel hexagonal packing. Similar bonding of the CN group is also suggested for the covalent cyanides of Pd (II), Pt (II), Ni (II) and Cu (II), which form four planar bonds, and their crystals are supposed to possess layer structures.

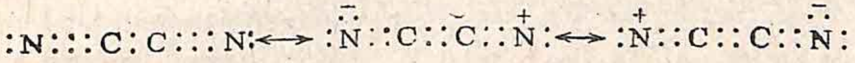
(iii) *Complex cyanides* : The CN^- ion is a good coordinating ligand and forms complexes with many transitional metals and also with the metals immediately following them (*e.g.* Zn, Cd, Hg). These complex cyanides have the composition $[M^{+x}(CN)_n]^{+x-n}$, where M^{+x} is the metal ion with $+x$ charge and n is the number of the CN group attached thereto. These are generally formed by treating a solution of the metal salt with excess of alkali cyanide solution (as in the formation of potassium ferrocyanide, potassium ferricyanide *etc.*), or by dissolving a heavy metal cyanide in alkali cyanide solution (as is the case with AgCN) : $FeCl_2 + 6\,KCN = K_4[Fe(CN)_6] + 2\,KCl$; $AgCN + KCN = K[Ag(CN)_2]$. The complexes have remarkable stabilities and their properties are completely different from those of the simple cations from which they are derived. Their formation is generally accompanied with remarkable change in the oxidation potential of the metal ions, and stabilization of certain unusual valence-state of the metal can often be effected by such reactions. In such complexes, the central metal ions are commonly 2–, 4–, 6– or 8–covalent.

The cyanides of alkali metals and of the alkaline earth metals are readily soluble in water and the aqueous solutions have strongly basic reaction due to hydrolysis, and they smell of hydrocyanic acid. The cyanides of heavy metals (except mercuric cyanide) are mostly insoluble in water, but are often soluble in excess of alkali metal cyanides to form complex salts.

Alkali metal cyanides are used in electroplating, extraction of metals (such as Au and Ag), in organic synthesis and also in qualitative chemical analysis.

Cyanogen $[(CN)_2]$: Cyanogen is generally prepared by heating mercuric cyanide : $Hg(CN)_2 = Hg + (CN)_2\uparrow$. A mixture of $Hg(CN)_2$ and $HgCl_2$ evolve the gas at much lower temperature : $Hg(CN)_2 + HgCl_2 = Hg_2Cl_2 + (CN)_2\uparrow$. It can also be prepared (although in a less pure state) by slightly heating a mixture of solutions of $CuSO_4$ and KCN. In this reaction, cupric cyanide, $Cu(CN)_2$, is formed as an unstable yollow coloured intermediate product which readily decomposes into white cuprous cyanide, $[Cu_2(CN)_2]$, and cyanogen : $CuSO_4 + 2\,KCN = K_2SO_4 + Cu(CN)_2$; $2\,Cu(CN)_2 = Cu_2(CN)_2 + (CN)_2\uparrow$. Cyanogen is a water-soluble, colourless gas. It has a distinctive smell and is highly poisonous. Cyanogen exhibits many characteristic properties of halogens, and as such, it is called a **pseudo-halogen.** Thus, like chlorine, it reacts with water (*hydrolysis*) to form hydrocyanic and cyanic acids : $(CN)_2+H_2O=HCN+HCNO$ (*cf.* $Cl_2+H_2O=HCl+HOCl$). Cyanogen is also absorbed by cold alkali solutions to form alkali cyanide and alkali cyanate : $(CN)_2+2\,KOH = KCN+KCNO+H_2O$ (*cf.* $Cl_2+2\,KOH = KCl+KOCl+H_2O$]. It is reduced by hydrogen to ethylenediamine : $(CN)_2+8[H] =H_2N.CH_2.\,CH_2.\,NH_2$. The gas burns in air with a reddish flame to form carbon dioxide and nitrogen : $(CN)_2+2O_2=2CO_2+N_2$.

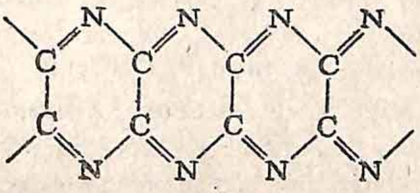
Cyanogen molecule is apparently linear. The structure of cyanogen is suppused to the resonance-hybrid of the following forms, with structure (I) making the greatest contribution.



$$:N:::C:C:::N: \longleftrightarrow :\overset{-}{\ddot{N}}::C::\overset{-}{C}::\overset{+}{N}: \longleftrightarrow :\overset{+}{N}::C::C::\overset{-}{\ddot{N}}:$$

(I) (II) (III)

At 400° – 500°C, cyanogen polymerizes to **paracyanogen,** $(CN)_n$, a solid material which reverts to cyanogen at 800° – 850°C, but decomposes above this temperature. The following structure has been suggested to the polymeric substance :



Cyanic acid and the cyanates : Cyanic acid (HCNO) is formed when an aqueous solution of potassium cyanate is acidified ; but the acid is completely decomposed by the water present to form ammonia and carbon dioxide : $KCNO+HCl=KCl+HCNO$; $HCNO+H_2O=NH_3+CO_2$.

Pure cyanic acid is a colourless liquid, and may be obtained by heating cyanuric acid $(CNOH)_3$.

Fused potassium cyanide reduces metallic oxides to the corresponding metals and potassium cyanate is formed. Thus, on slowly adding lead monoxide or red lead to a well-stirred fused mass of KCN, metallic lead and potassium cyanate are formed : $KCN+PbO=KCNO+Pb$; $4KCN+Pb_3O_4=4KCNO+3Pb$. The cooled mass is extracted with hot aqueous alcohol, and the extract is concentrated to get the crystals of potassium cyanate. Sodium cyanate may be similarly prepared.

Ammonium cyanate (NH_4CNO) is obtained by mixing concentrated solutions of potassium cyanate and ammonium chloride: $KCNO+NH_4Cl=NH_4CNO+KCl$.

The cyanates are slowly hydrolysed in aqueous solution to form the corresponding metal carbonate and ammonium carbonate: $2KCNO+4H_2O=K_2CO_3+(NH_4)_2CO_3$. Ammonium cyanate (or a mixture of KCNO and NH_4Cl) is readily converted on heating into the isomeric compound, urea: $NH_4CNO=CO(NH_2)_2$. [This reaction, discovered by Wohler in 1828, definitely shattered the hypothetical barrier between 'inorganic' and 'organic' substances.]

Thiocyanic acid and thiocyanates: Thiocyanic acid (HSCN) is obtained as a pungent-smelling gas when mercury thiocyanate (or lead thiocyanate) is warmed in a stream of hydrogen sulphide: $Hg(SCN)_2+H_2S=HgS+2HSCN$. The compound can also be prepared as a gas on heating potassium thiocyanate (KSCN) with potassium bisulphate: $KSCN+KHSO_4=K_2SO_4+HSCN$.

Thiocyanic acid is a colourless, oily, non-poisonous and very volatile liquid. In the pure state, it is extremely unstable and decomposes with the formation of HCN and some other solid product of complex nature. It is stable at very low temperature and in dilute ($<5\%$) solution. It is a strong acid and is completely miscible with water. The aqueous solution of the acid is easily prepared by treating metal thiocyanates with dilute acids.

The salts of thiocyanic acid are called *thiocyanates or sulphocyanides*. They are readily formed by the direct union of metal cyanides and sulphur at elevated temperatures. Thus, potassium thiocyanate is prepared by fusing KCN with powdered sulphur, extracting the cooled melt with alcohol and crystallising the product from the alcoholic solution: $KCN+S=KSCN$. Ammonium thiocyanate is obtained through the reaction between ammonium cyanide and yellow ammonium sulphide solution: $NH_4CN+(NH_4)_2S_2=NH_4SCN+(NH_4)_2S$. It is technically prepared by the action of aqueous ammonia on CS_2 at about 110°C and under-pressure: $2NH_3+CS_2=NH_4SCN+H_2S$.

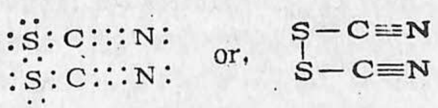
Most thiocyanates are soluble in water; silver, mercury and copper (I) thiocyanates are insoluble and lead thiocyanate is sparingly soluble in water. The thiocyanates of colourless cations are also colourless. They resemble metallic chlorides in giving a precipitate of silver thiocyanate (insoluble in water and dil. acids), when their aqueous solutions are treated with $AgNO_3$ solution: $AgNO_3+KSCN=AgSCN\downarrow+KNO_3$. [This reaction is taken advantage of in the volumetric estimation of silver by *Volhard's method.*] A characteristic and very sensitive reaction of thiocyanates is the formation of red colour when their aqueous solutions are added to ferric chloride solution. The blood-red colour is due to the formation of complex $Fe(SCN)_6^{3-}$ ions : $Fe^{+3}+6SCN^- \rightleftharpoons Fe(SCN)_6^{3-}$. [It is a very sensitive test of Fe^{+3} and SCN^-.] Thiocyanates are decomposed by moderately concentrated sulphuric acid : $KSCN+2H_2SO_4+H_2O=COS+(NH_4)HSO_4+KHSO_4$.

Thiocyanates are used in dyeing. Ammonium and potassium thiocyanates are used as reagents for the detection of ferric salts and for the estimation of silver.

Thiocyanogen $(SCN)_2$: Thiocyanogen was first obtained (1919) by the action of bromine (dissolved in CS_2) on silver thiocyanate : $2AgSCN+Br_2=2AgBr+(SCN)_2$. Oxidation of thiocyanates with lead tetraacetate or MnO_2 also produces the substance. Crystallisation of concentrated solution of thiocyanogen in ethyl bromide or diethyl ether at −70°C gives solid thiocyanogen, melting at −2° to −3°C. Cryoscopic measurements in bromoform solutions of thiocyanogen give molecular weight corresponding to the dimeric formula, $(SCN)_2$. It is more or less stable as solutions in certain solvents ; but, in the free state, it rapidly polymerizes irreversibly to a brick-red solid, called *parathiocyanogen*, $(SCN)_n$, of unknown structure.

Thiocyanogen is a *pseudo-halogen.* Free thiocyanogen closely resembles iodine in its chemical behaviour. Thus, it combines with metals and has almost the same oxidising powder as iodine : $M+(SCN)_2=M^{+2}+2SCN^-$: It liberates iodine from iodides, and is itself set free by excess of iodine : $2I^-+(SCN)_2 \rightleftarrows I_2+2SCN^-$. It reacts with thiosulphate to give thiocyanate and tetrathionate : $(SCN)_2+2S_2O_3^{2-}=2SCN^-+S_4O_6^{2-}$. It liberates sulphur from hydrogen sulphide : $(SCN)_2+H_2S=2H^++2SCN^-+S$.

The structure of thiocyanogen has been suggested as shown below, and such a structure is in good agreement with its properties :



Carbides : The binary compounds of carbon with elements of lower or about equal electronegativity are known as carbides. Such a definition of this class of compounds obviously exclude the binary compounds of carbon with oxygen, sulphur, nitrogen, phosphorus, halogens *etc.* Although methane and other hydrocarbons necessarily fall within the category of carbides by the above definition, these are conventionally dealt with in the subject-matter of organic chemistry.

Carbides vary widely in their properties which are dependent on the type of linkage present in their molecules. They are, therefore, classified as (i) **ionic** or **salt-like carbides**, (ii) **covalent carbides** and (iii) **interstitial** or **metallic carbides.**

(i) *Ionic or salt-like carbides* : These are formed chiefly by the metals of Groups I, II, and III of the Periodic Table. They form colourless, transparent crystals and are decomposed by water or dilute acids at ordinary temperatures to produce hydrocarbons like methane or acetylene or allylene (methyl acetylene). These carbides are, therefore, further sub-divided into three categories, *viz.* **methanides, acetylides** and **allylides,** according as their crystals contain the discrete C^{-4} groups, C_2^{2-} groups and C_3^{4-} groups respectively.

(*a*) *Methanides.*—Carbides of this category yield methane on treatment with water or dilute acids and they are, therefore, considered as the derivatives of methane. The important examples of such carbides are beryllium carbide (Be_2C) and aluminium carbide (Al_4C_3).

$Be_2C+2H_2O=2BeO+CH_4$; $Al_4C_3+12H_2O=4Al(OH)_3+3CH_4$.

(*b*) *Acetylides.*—These carbides produce, completely or predominatly, acetylene on hydrolysis. Metals of Group I of the Periodic Table (both the alkali metals and the coinage metals) form carbides M_2C_2 (M=Li, Na, K, Rb, Cs, Cu, Ag and Au) ; the metals of Group II form carbides MC_2 (M=Be, Mg, Ca, Sr, Ba, Za, Cd) ; of the metals of Group III, aluminium and cerium form carbides Al_2C_6 and Ce_2C_6 ; the lanthanons form carbides MC_2 (M=Y, La, Ce, Pr, Nd). Some other acetylides, having the metals in unusually low oxidation states, *viz.* ThC_2, UC_2 and VC_2 are also known.

$CaC_2+2H_2O=Ca(OH)_2+C_2H_2$; $Al_2C_6+6H_2O=2Al(OH)_3+3C_2H_2$.

(*c*) *Allylides.*—The only carbide of this class is the magnesium carbide, Mg_2C_3, which is formed when the acetylide MgC_2 is heated. It gives allylene (methyl acetylene) on hydrolysis : $Mg_2C_3+4H_2O=2Mg(OH)_2+CH_3C\equiv CH$.

The ionic carbides are generally prepared by heating the metal or its oxide with carbon at elevated temperatures, or by the action of acetylene on the compounds of the metals (*e.g.* of Cu, Ag, Au, Zn, Cd). Lithium carbide (Li_2C_2) is formed by the direct combination of the metal with carbon, but the corresponding carbides of the other alkali metals are formed by heating the metals in acetylene gas. K, Rb and Cs carbides can also be prepared by passing acetylene into a solution of the respective metal in liquid ammonia.

(ii) *Covalent carbides*: The two elements, silicon and boron, which approach carbon closely in size and electronegativity, form truly covalent carbides. Silicon carbide or carborundum (SiC) is a hard, infusible and chemically stable substance, which is prepared by reducing silica with carbon in an electric furnace (also see in '*compounds of silicon*' described later in this chapter). It is a giant molecule of three-dimensional structure, in which carbon and silicon atoms alternate and each is tetrahedrally surrounded by four atoms of the other kind. The breakage of such a structure would require the rupturing of a large number of covalent bonds, and this explains its extreme hardness, chemical inertness and the very high decomposition temperature.

Boron carbide, B_4C, is also an extremely hard, influsible and chemically inert substance, and is prepared by reducing boron trioxide (B_2O_3) with carbon in an electric furnace. The structure of boron carbride is somewhat peculiar, and consists of structural units of linear chains of three carbon atoms and the boron atoms in icosahedral groups of twelve, packed together in NaCl-like arrays. Such a structure explains its above properties, as well as its appreciable electrical conductivity.

(iii) *Interstitial or metallic carbides*: These carbides are formed by the transition metals of Groups IVA, VA, and VIA of the Periodic Table. Of these metals, Ti, Zr, Hf, V, Nb, Ta, Mo and W form carbides of the composition MC, while V, Mo and W forms compounds M_2C also (where M=the metal concerned). The carbon atoms in these carbides occupy octahedral holes in the cubical or hexagonal close-packed metal-lattices and consequently, the free electron structure and other characteristic properties of the pure metal are not fundamentally affected. The insertion of carbon atoms in these rather stabilises the crystal-lattice. The important properties of these carbides, *viz*. the very high melting points

(3000°–4800°C), great hardness (9–10 in Moh's scale) and superior electrical conductivity etc. thus find easy explanation from such structures. Provided that the radius of the metal atoms is greater than about 1·3Å, the carbon atoms can enter the metal-lattice without distorting it. The metals Cr, Mn, Fe, Co and Ni have atomic radii less than 1·3Å. Hence, in the carbides of these metals (Cr_3C_2, Fe_3C, Mn_3C, Co_3C and Ni_3C), the metal-lattice is distorted. These carbides exhibit properties which are intermediate between ionic and true interstitial carbides. They are hydrolysed by water or dilute acids to form a mixture of hydrocarbons and hydrogen : $Mn_3C + 6H_2O = 3Mn(OH)_2 + CH_4 + H_2$. The structure of these carbides contains chains of carbon atoms running through the distorted metal-lattice.

The interstitial carbides are generally prepared by the direct union of metal and carbon, or by the reduction of the oxide of the metal by carbon at about 2200°C. Powdered carbides, thus obtained are compacted by suitable methods of powder metallurgy. Many interstitial carbides are used in high-speed cutting tools and as abrasive.

FUELS

Production of heat is necessary in our everyday life for many domestic purposes, movement of vehicles and also in factories. Various combustible substances, gaseous, liquid or solid, which are burnt for these purposes, are called fuels. These always contain carbon, and usually hydrogen as well.

Fuels may be of *organic* or *inorganic* origin. Organic fuels include wood, peat, lignite, bituminous coal and anthracite, charcoal, coke, dried cow-dung, industrial gases, *gobar gas* (prepared from raw cow-dung), crude petroleum and its products, benzol, methanol, ethanol, natural gases *etc.*. Inorganic fuels like sulphur, phosphorus, silion and aluminium are sometimes used in metallurgy and industry. It may be seen from the above list that many of the organic fuels named are natural raw materials, while some others are manufactured from them.

Fuels	Solid	Liquid	Gaseous
I. Natural raw materials.	Wood, Peat, Lignite, Bituminous coal, Anthracite.	Crude Petroleum.	Natural gases.
II. Processed or manufactured products.	Coke, Charcoal.	Gasoline, diesel, kerosene, benzol, methanol, ethanol *etc.*	Coal-gas, water-gas, producer gas, oil gas *etc.*

Solid fuels are commonly used in domestic ovens, metallurgical furnaces, steam-ships and steam-engines. Liquid fuels are used to produce locomotive power in automobiles, aeroplanes, modern railway engines and ships. (kerosene is used in stoves and lamps). Gaseous fuels are used in industries and also in laboratories and kitchens.

Calorific value of fuels : The quality of a fuel is judged by its *calorific value*, which is measured by the maximum amount of heat in B. Th. U. (British thermal unit) evolved by the complete combustion of 1 lb. of the solid or the liquid fuel or 1 Cu-ft. of the gaseous fuel. [1 B. Th. U. of heat is the quantity of heat that is required to raise the temperature of 1 lb. of water through 1°F.] Higher the calorific value of a fuel, better it is for practical purposes. The calorific value of bituminous coal is 14950 B. Th. U. ; that of coal-gal is 560 B. Th. U. Another important consideration in the use of a fuel is the highest temperature attainable in its combustion (*Pyrometric effect*). Gaseous fuels have highest pyrometric effect, as they burn completely with theoretical amount of air.

Gaseous fuels : The use of gaseous fuels like the natural gases, coal-gas, producer gas. water-gas, oil gas *etc.* have the following advantages over the solid and liquid fuels : (i) they can be produced at the site of the use (except the natural gases) in many cases, so that the trouble of transport is much minimised ; (ii) their products of combustion are also gaseous and thus requires little effort for disposal ; (iii) they can be easily handled during operation and the temperature of furnance can be effectively controlled by regulating the rate of their flow and combustion and (iv) they have high pyrometric effect.

The natural gases.—These are obtained from petroleum-wells and consist of a mixture mainly methane and some other saturated gaseous hydrocarbons of low molecular weights, along with small amounts of H_2, N_2, CO_2 *etc.* They are either directly transported through pipe-lines to the actual place of use or are marketed in portable cylinders as *liquefied petroleum gas* (L. P. G.), after compressing in small amounts of liquid petroleum. Gases obtained by the fermentation of sewage sludge or raw cow-dung (*Gobar gas*) are also being put into use as fuel.

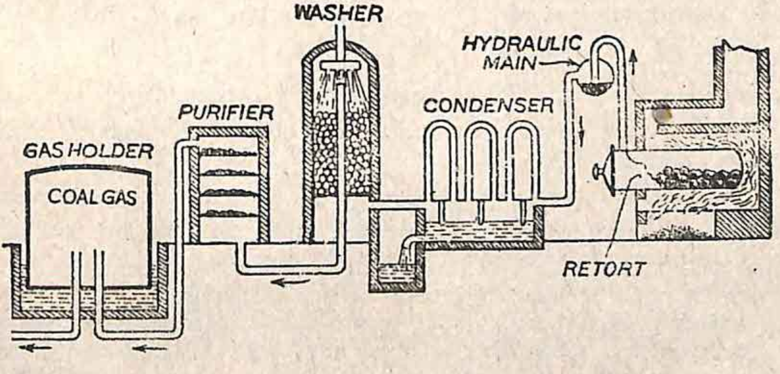
Carbonisation of coal.—The process of obtaining coke through destructive distillation of coal is known as the *carbonisation of coal* The destructive distillation of coal not only gives coke, but it also produces a volatile fraction which consists of gases and liquids. The mixture of gases is commonly known as coal-gas, which is mainly used as a gaseous fuel, and the liquid distillate contains ammoniacal liquor and coal-tar.

Among the different varieties of coal available in nature, generally the bituminous coal is used in the destructive distillation process. Carbonisation is effected either at lower temperatures (600°—700°C) or at higher temperatures (1200°—1400°C). The low temperature carbonisation of coal gives smaller amount of coal gas (4000—6000 cu. ft./ton) of higher calorific value, while the high temperature carbonisation gives larger amount of coal gas (12000—15000 cu. ft./ton) of lower calorific value. The amount of coke produced is also higher in the former process, although it contains larger percentages of volatile matters. The amounts of coal tar and light oil are higher and that of ammonical liquor lower in the former process than those in the latter process. The coke obtained in the low temperature carbonisation is called *soft coke* and it is generally used for domestic purposes. It burns smoothly and without any smoke. The coke obtained through high temperature carbonisation of coal is called *hard coke*. It forms smoke while burning, and is generally used in metallurgy.

Coal gas : Coal gas is a mixture of mainly combustible gases, together with some nitrogen, carbon dioxide and oxygen (inert diluents) and some impurities like hydrogen sulphide). The composition of coal gas is variable, depending upon the nature of the coal and the condition of its carbonisation. An average composition of a representative sample may be as shown below :

Hydrogen	— 50% by volume	Combustible, heat-producing, but non-illuminant gases.
Methane	— 30% " "	
Carbon monoxide	-- 8% " "	
Ethylene, acetylene, benzene, naphthalene.	3% " "	Illuminants.
N_2, O_2, CO_2	— 5% " "	— Inert diluents.
H_2S, HCN *etc.*	— Small amounts, if present.	Inpurities.

Coal gas is manufactured by the high temperature carbonisation (1200° – 1400°C) or destructive distillation of bituminous coal. Small lumps of coal are distilled in a series of horizontal or vertical fire-clay retorts by the heat produced through burning of producer gas externally. The volalite products of distillation escape through a vertical iron *ascension pipe* fitted to the month of each retort, and these pipes lead to a long horizontal tube, half-filled with water, called the *hydraulic main.* The ascension pipes deliver the gases under water, so that the hydraulic main serves as a water-seal between the retorts and the rest of the plant, and thus the retorts can be opend safely for re-charging. At the temperature prevailing in the hydraulic main, some portion of tar and ammonia present in the distillation products are separated here and the crude coal-gas then passes over through a series of *iron-pipe condensers* cooled by air. More tar and ammonical liquor are condensed here and are collected in the *tar well* (placed below the condensers) in two separate layers—the lower heavy layer of coal-tar and the upper lighter layer of ammonical liquor. The mixture of gases is then sucked by an air-pump (not shown in the figure) to maintain its flow towards the gas-holder and is allowed to pass successively through a *tar-separator*, a *washer* or scrubber, a *purifier*, and is finally stored in large *gas-holders* made of iron-sheets. The *washer* or the *scrubber* is a vertical iron-tank, packed with coke. A stream of water trickles down through the packing from above, and the gas-mixture passes up the tank. Here the gas-mixture is freed from last traces of ammonia and tar. The



Coalgas manufacture

purifier is an iron-box, containing moist ferric oxide on its shelves. On passing through the *purifier*, the H_2S contained in the gas-mixture is practically fully removed: $2Fe(OH)_3+3H_2S=Fe_2S_3+6H_2O$. [When the ferric oxide is exhausted through absorption of H_2S, it can be *revivified* by exposing to moist air and used again : $2Fe_2S_3+3O_2+6H_2O=4Fe(OH)_3+6S$. But, in such a process, when the free-sulphur-content of ferric oxide exceeds 50%, it becomes unsuitable as a purifier, and is then disposed of as the 'spent oxide of iron' for the manufacture of H_2SO_4.] Carbon disulphide, when present in appreciable amounts in the coal-gas, is removed by passing over finely divided nickel catalyst (heated at 400°C). Carbon disulphide reacts under this condition with the hydrogen present in coal-gas to form H_2S, which is removed by moist ferric oxide or slaked lime : $CS_2+2H_2=C+2H_2S$. Hydrocyanic acid, present in the coal-gas, is removed as sodium ferrocyanide by passing it through ferrous sulphate and caustic soda contained in a purifier : $FeSO_4+6HCN+6NaOH=Na_4[Fe(CN)_6]+Na_2SO_4+6H_2O$.

Coal-gas is colourless, with a peculiar bad smell and reducing properties. Its calorific value is about 560 B. Th. U./Cu. ft. It is widely used in gas-burners in laboratories and as a domestic and industrial fuel.

By-products of the coal-gas industry : The coal-gas industry produces a number of useful by-products. These are : *Coke, coal-tar, ammoniacal liquor gas-carbon* and *spent oxide of iron.*

(1) **Coke :** The solid residue left in the retorts during the manufacture of coal-gas is coke, which is largely used as domestic and industrial (including metallurgy) fuel.

(2) **Coal-tar :** This is the black, viscous liquid, collected in the hydraulic main and the tar-well. Coal-tar is the source of a large number of organic aromatic compounds used as solvents or for the manufacture of dyes, drugs, explosives, perfumes, insecticides, fungicides *etc.* Coal-tar is itself used as a wood-preservative, and for water-proofing gunny bags and wrapping papers. *Pitch*, obtained as the residue of the distillation of coal-tar, is used for road-making.

(3) **Ammoniacal liquor :** The liquid, obtained in the hydraulic main and as the upper layer in the tar-well, is known as the ammoniacal liquor. It gives ammonia on boiling with slaked lime, and thus provides the starting material for the manufacture of fertilizers like ammonium sulphate and ammonium phosphate.

(4) **Gas-carbon :** This is formed as hard, black deposits on the inner walls of the retorts as a result of thermal decomposition of some of the gaseous hydrocarbons produced during the manufacture of coal-gas. It is generally used for making electrodes.

(5) **Spent oxide of iron :** This is formed in the purifiers through the absorption of H_2S by moist iron oxide and it cannot be revived any longer to be used again in the process. It contains free sulphur, along with Fe_2S_3 and some cyanogen compounds. This is used for the production of SO_2 for the manufacture of H_2SO_4 and also for the preparation of ferrocyanides.

Producer Gas.

The producer gas (or the air-gas, as it is sometimes called), is a very useful industrial fuel. It is a mixture of mainly carbon monoxide and nitrogen, together with small amounts of hydrogen, methane and carbon dioxide and is manufactured by passing air through incandescent coke at about 1000°C. The composition of producer gas varies according to the condition of its preparation, and an average volume-composition of a representative sample may be as follows : $H_2=6\%$, $CH_4=8\%$, $CO_2=4\%$, $CO=20\%$ and $N_2=62\%$.

The gas is manufactured in a closed steel furnace, called the **producer** (Fig. 15·4), which is lined inside with fire-bricks. Heated coke are placed on iron-grating inside the producer and a blast of air is passed through the layers of coke from the bottom. Oxygen in the air oxidises coke into CO and CO_2 near the bottom. These oxidation reactions, being highly exothermic, produce much quantity of heat : $2C+O_2=2CO+58$ Kcals. ; $C+O_2=CO_2+97$ Kcals. The hot mixture of gases travels up the furnace, where CO_2 is reduced by coke to CO at the higher temperature (~1000°C) prevailing there, the reaction being endothermic : $CO_2+C=2CO-39$ Kcals. The bed of coke is maintained at high temperature, as the proportion of CO increases with the increase of temperature. The hot gases leave the furnace through the exit near its top and is directly led to the furnace required to be heated by its burning. [For this reason, producers are generally built near the site of the use of the

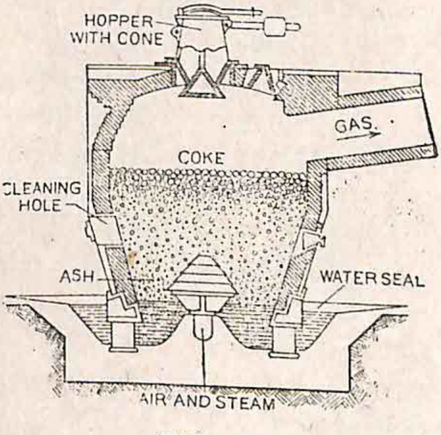


Fig. 15·4

gas.] The hot producer gas is burnt as a fuel in furnaces by admixing with it fresh quantites of air, when CO in it is oxidised to CO_2 and produce much heat. The air used in gas-producers during the manufacture of producer gas is called the *primary air*, while that admixed with it for its burning is called the *secondary air*. Coke is charged in the producers from the top by means of a hopper with cup-and-cone arrangement and the produced ash is withdrawn through the cleaning hole.

Producer gas is used as a fuel in many industrial furnaces (such as in metallurgy, glass-making, coal-gas manufacture *etc*.). Its calorific value is about 150 B.Th.U./Cu. ft.

Water-gas : An useful industrial fuel and the starting material of many important syntheses and large-scale production of hydrogen, water-gas is mainly a mixture of almost equal volumes of hydrogen and carbon monoxide, admixed with small amounts of methane, carbon dioxide and nitrogen. It is manufactured in a way simialr to the preparation of producer gas, by blowing steam through incandescent coke at about 1000°C in a producer already described (Fig. 15·4). Steam reacts with coke at the elevated temperature to form CO and H_2 (*water-gas reaction*) : $C+H_2O \rightleftharpoons CO+H_2-39$ Kcals. The reaction is highly endothermic, resulting in cooling of the hot coke-bed as it progresses. When the temperature of the coke-bed falls below 1000°C, the reaction between steam and coke produces carbon dioxide according to another endothermic reaction, $C+2H_2O=CO_2+2H_2-29$ Kcals. This further lowers the temperature of the coke-bed. Thus, the proportion of CO_2, which has no calorific value, increases with the decrease of temperature of the bed. To overcome this defect, the blowing of steam is continued for 6-8 minutes (*make-period*) and is then stopped, while a stream of air is blown in for about 2 minutes (*blow-period*). This operation ensues the exothermic reaction that produces air-gas (producer gas) and the temperature of the bed again rises to allow the occurrence of water-gas reaction. [The producer gas, thus formed, is generally turned to waste.] Thus, the blowing of steam and air alternates and water-gas is continuously formed.

Water-gas is used as a fuel and a reducing agent in metallurgy. It is also the starting material for the production of hydrogen and methanol on a large scale. It burns with a pale blue flame and has a calorific value of 300 B. Th. U./Cu. ft.

Semi-water gas: A mixture of water gas and producer gas in known as *semi-water gas.* Its average volume-composition is : $CO=30\%$, $H_2=12\%$, $CH_4=3\%$, $CO_2=2\%$ and $N_2=53\%$. It is manufactured by continuously blowing a mixture of steam and air through a bed of incandenscent coke in a gas-producer. The amount of steam and air in the mixture is so adjusted that the heat of the coke-bed lost by the endothermic water-gas reaction is just balanced by the exothermic producer gas reaction.

Semi-water gas is used as the source of N_2 and H_2 for the synthesis of ammonia by Haber's process. It is also used as a fuel, having a calorific value of 180 B.Th.U./Cu. ft.

Carburetted water-gas: Water-gas alone burns with a blue non-limuninous flame and it has no illuminating power. To make it useful for illuminating purposes, it is mixed with various hydrocarbons, partly unsaturated, obtained from cracked oil-gas, and the mixture is known as **carburetted** (enriched) **water gas.** It is manufactured by passing water-gas from the gas-producer successively through two towers packed with chequer-brickworks (fig. 15:5). The first tower is called the **carburetter** and the second is called the **superheater.** These are first heated to redness by burning producer gas. In the carburetter, a spray of mineral oil is injected from the top. The mixture of water-gas and vaporised oil then passes through the red-hot packing of the superheater, where the oil-vapours are thermally decomposed (or *cracked*), with the formation of permanent gases rich in ethylene. The mixture of gases, passing out of the superheater, is then purified by scrubbing in the **purifier** and collected.

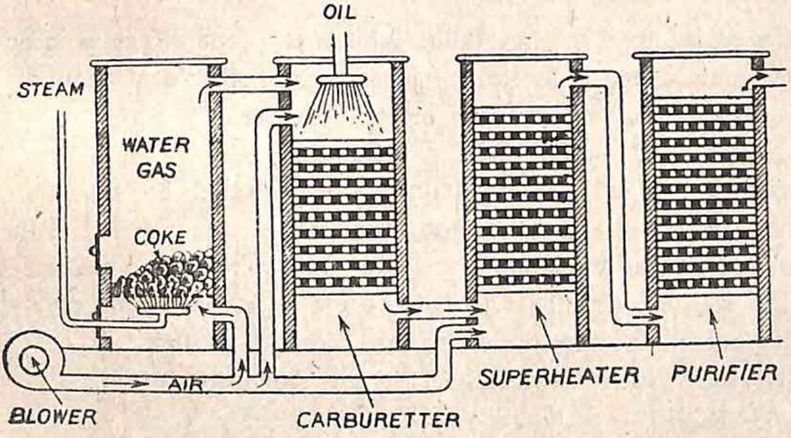


Fig. 15·5

Oil-gas: Mineral oils like petrol, kerosene *etc.* undergo thermal decomposition into a mixture of gaseous hydrocarbons, when they are allowed to fall dropwise on any red-hot surface of iron. This is generally used in laboratory burners where coal-gas is not available.

SILICON

Symbol : Si ; *Atomic number*=14 ; *Atomic weight*=28·09.
Electronic configuration : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$.

Occurrence : Silicon is second only to oxygen in its abundance in earth's crust (28% by weight). It never occurs free in nature, but in combination as silica or silicates, the element is widely distributed in sand, rocks, clays and minerals. As the dioxide, SiO_2, it occurs in **sand, quartz, flint** and **agate.** As silicate, it is the constituent of **felspar** ($KAl\,Si_3O_8$), **kaolinite** ($H_2Al_2Si_2O_9$), **mica** [$KH_2Al_3(SiO_4)_3$], **asbestos** [$Mg_3Ca(SiO_3)_4$]. Clays are formed by the atmospheric weathering of felspar in the igneous rocks.

Silicon does not exhibit allotropy. It is known in only one crystalline octatedral form. Silicon is sometimes obtained as the so-called *amorphous* form, which is nothing but the aggregate of minute octahedral crystals similar to the large crystals of the crystalline silicon just mentioned.

Preparation : (1) Crystalline silicon is prepared as a grey (or light yellow) mass by heating a mixture of silica and finely divided coke or calcium carbide in an electric furnace.

$$SiO_2+2C=Si+2CO\uparrow\ ;\ SiO_2+CaC_2=Si+Ca+2CO\uparrow$$

Relatively pure crystalline silicon can be obtained by the aluminothermic reduction of potassium fluosilicate. [It is essential that an excess of aluminium is employed, since this acts in the molten state as the solvent for silicon.] On cooling the mass, silicon crystallises out from molten aluminium in the form of leaflets. The crystals are treated with HCl to remove the adhering aluminium.

$$3K_2SiF_6+4Al=3Si+6KF+4AlF_3.$$

(2) Amorphous silicon is prepared by heating to red-heat, a perfectly dry mixture of finely ground silica and magnesium powder (taken in a fireclay crucible) in an electric furnace.

$$SiO_2+2Mg=Si+2MgO.$$

[To prevent too violent a reaction, the reacting mixture is diluted with about $\frac{1}{4}$th of its amount of MgO. An excess of magnesium should be avoided to prevent the formation of magnesium silicide.]

The product, after cooling, is leached with dilute HCl (to remove MgO) and is then heated with hydrofluoric acid to remove any unchanged silica. Amorphous silicon is thus obtained as a brown powder.

Amorphous silicon may also be prepared by passing vapours of silicon tetrachloride ($SiCl_4$) over heated sodium or potassium, and washing the cooled mass with water to remove the alkali halides : $SiCl_4+4Na=Si+4NaCl$.

When amporphous silicon is dissolved in molten aluminium and the melt is allowed to crystallise, crystalline silicon results.

Properties : Amorphous silicon is a light-brown to dark-brown hygroscopic powder (sp. gr.=2·35), while crystalline silicon is light yellow to brown octahedral crystals with metallic lustre (sp. gr.=2·5). The amorphous variety of silicon is more reactive than the crystalline variety. The element is definitely a non-metal, forming acidic oxide (SiO_2), but having metallic lustre and metallic conductivity in the crystalline form. Amorphous silicon vigorously burns in air or oxygen, when heated, to form silicon dioxide ; but, crystalline silicon is unaffected when so heated. Silicon is not soluble in, nor does it react with water at ordinary temperatures. But, red-hot silicon decomposes steam : $Si+2H_2O=SiO_2+2H_2$. Silicon burns in fluorine spontaneously, and with chlorine at about 300°C, to form the corresponding tetrahalides : $Si+2F_2=SiF_4$; $Si+2Cl_2=SiCl_4$. These halides are readily hydrolysed by water to give hydrohalic acid and orthosilicic acid : $SiCl_4+4H_2O=4HCl+H_4SiO_4$. Silicon is not acted upon by any single acid ; but, a mixture of nitric and hydrofluoric acids dissolves it, with the formation of hydrofluosilicic acid : $Si+6HF=2H_2+H_2SiF_6$. Silicon reacts very readily with caustic alkalis, even when these are very dilute, to form alkali silicates : $Si+2NaOH+H_2O=Na_2SiO_3+2H_2$. When fused with sodium carbonate, sodium silicate is formed, with the separation of carbon particles : $Si+Na_2CO_3=Na_2SiO_3+C$. It combines with many metals, when heated at high temperatures in an electric furnace in absence of air, to form metal silicides : $2Mg+Si=Mg_2Si$. [Magnesium silicide produces a mixture of silicon hydrides, *e.g.* silicomethane (SiH_4), silicoethane (Si_2H_6) *etc.*, when treated with HCl in absence of air : $Mg_2Si+4HCl=2MgCl_2+SiH_4$.]

Uses : Silicon is used in preparing acid-resisting steel, bronzes, ferro-silicon *etc.* It is also used as a semiconductor in transistors.

Compounds of silicon.

Silicon Hydrides : Silicon hydrides are commonly called the *silanes* and their stoichiometries are analogous to those of the paraffin hydrocarbon, C_nH_{2n+2}. But, although the paraffins are practically limitless in number, only a few silanes exist due to the relative weakness of the Si−Si bond. The disposition of the bonds around the silicon atoms in silanes is tetrahedral.

A mixture of silanes is obtained by hydrolysing magnesium silicide (prepared by heating a mixture of powdered silicon and magnesium in absence of air) with sulphuric acid or phosphoric acid (Stock and co-workers, 1916). The mixture contains six silanes in the approximate proportions : 40% SiH_4 (mono-silane), 30% Si_2H_6 (di-silane), 15% Si_3H_8 (tri-silane), 10% Si_4H_{10} (tetra-silane) and 5% Si_5H_{12} (penta-silane) and Si_6H_{14} (hexa-silane), together with traces of higher silanes. The products can be separated by fractional distillation.

Monosilane is best prepared in the pure state by the action of lithium aluminium hydride on silicon tetrachloride in ether solution : $LiAlH_4+SiCl_4=SiH_4+LiCl+AlCl_3$. Disilane is analogously prepared from Si_2Cl_6.

$$2Si_2Cl_6+3LiAlH_4=3LiCl+3AlCl_3+Si_2H_6.$$

All the silanes are colourless—monosilane and disilane being gases, while the other silanes are liquids. Their boiling points increase steadily with the increase of molecular weight. They are very reactive and spontaneously inflammable in air (sometimes with explosive violence). Their thermal stabilities are much lower than the corresponding hydrocarbons, and it decreases with the increasing molecular weight and also on exposure to ultra-violet light. Silanes are stable towards neutral or acidulated water, but they are readily hydrolysed by traces of alkali (even that is provided by glass vessels) to produce sodium silicate and hydrogen :

$$SiH_4+2NaOH+H_2O=Na_2SiO_3+4H_2 \; ; \; Si_2H_6+4NaOH+2H_2O =2Na_2SiO_3+7H_2.$$

The silanes are strong reducing agents and reduce copper sulphate to copper silicide, and silver nitrate to metallic silver :

$$2CuSO_4+SiH_4=Cu_2Si+2H_2SO_4 \; ; \; 4AgNO_3+SiH_4 =4Ag+Si+4HNO_3.$$

They react explosively with halogens even at the room temperature.

Unlike the paraffin hydrocarbons, the silanes react with hydrogen chloride or bromide at 100°C in the presence of the corresponding aluminium halide (catalyst), when successive replacement of hydrogens by halogens takes place, and products like SiH_3X, SiH_2X_2 ($X = Cl$ or Br) *etc.* are formed : $SiH_4 + HCl = SiH_3Cl + H_2$; $SiH_3Cl + HCl = SiH_2Cl_2 + H_2$ *etc.* Many important alkyl- and aryl-silanes are also known.

Silicon dioxide or Silica (SiO_2) : Silicon dioxide occurs abundantly in nature as a crystalline solid in the form of quartz, sand *etc.*, and it is the principal constituent of all silicate minerals and rocks. It also occurs in small quantities in plants and animals.

Unlike the carbon atom, silicon cannot form double bonds, and as such, SiO_2 cannot exist as a discrete molecule like CO_2, but forms giant molecules of an infinite three-dimensional structure (fig. 15·6). [This explains why CO_2 is a gas, while SiO_2 is a high-melting solid.] Crystalline silica exists in three different forms, *viz.* quartz, tridimyte and crystobalite. In all these forms, each silicon atom is tetrahedrally surrounded by, and bound to four oxygen atoms through single bonds (the Si—O bonds being considerably ionic in character) and each oxygen atom is common to two tetrahedra. Each of these three forms has a low-temperature and a high-temperature modifications.

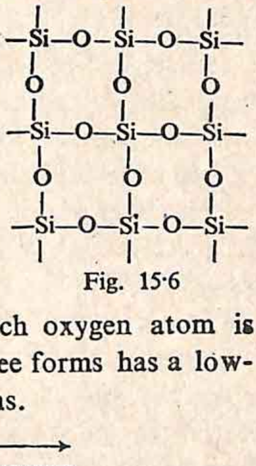


Fig. 15·6

←——— High-temperature modifications ———→

$$\begin{tikzcd}
\beta\text{-Quartz} \arrow[r, shift left, "870^\circ\text{C}"] \arrow[d, shift left] & \beta\text{-Tridymite} \arrow[l, shift left] \arrow[r, shift left, "1470^\circ\text{C}"] \arrow[d, shift left] & \beta\text{-Crystobalite} \arrow[l, shift left] \arrow[r, shift left, "1710^\circ\text{C}"] \arrow[d, shift left] & \text{Liquid silica} \arrow[l, shift left] \\
\alpha\text{-Quartz} \arrow[u, shift left, "573^\circ\text{C}"] & \alpha\text{-Tridymite} \arrow[u, shift left, "120-160^\circ\text{C}"] & \alpha\text{-Crystobalite} \arrow[u, shift left, "200-275^\circ\text{C}"] &
\end{tikzcd}$$

←——— Low-temperature modifications ———→

The structural arrangement in quartz and tridymite is helical, and since a helix may be either left-handed or right-handed, these two crystalline forms exhibit optical isomerism.

Of all the crystalline forms of silica, quartz is the most stable (others are metastable at ordinary temperatures). It is a colourless and hard substance (sp. gr.=2·65). Many varieties of quartz occur naturally in beautiful colours due to the presence of small quantities of impurities. These are used as gem-stones like *jasper* (red), *amethyst* (purple), *opal* (white) and *agate*.

Silica can also be prepared in the amorphous form by hydrolysing silicon tetrachloride to gelatinous silicic acid (or hydrous silica) and then drying and igniting the product. This can also be obtained by the addition of mineral acids to solution of alkali metal silicates (obtained by fusing silica or a silicate mineral with Na_2CO_3, and extracting the cooled melt with water) and then processing the precipitated hydrous silica as above : $SiO_2 + Na_2CO_3 = Na_2SiO_3 + CO_2$; $Na_2SiO_3 + 2HCl = H_2SiO_3 + 2NaCl$; $H_2SiO_3 = SiO_2 + H_2O$. Amorphous silica forms fine white powder.

Slow cooling of molten silica, or heating any form of silica to the softening temperature gives a vitreous, glassy mass which is amorphous.

Silica, in any form, is rather unreactive at ordinary temperatures towards hydrogen, chlorine, bromine, most acids and metals. It is also insoluble in water. Silica is, however, attacked by fluorine, hydrofluoric acid and alkalis. With HF, silica readily forms volatile silicon tetrafluoride which is hydrolysed by water to silicic acid : $SiO_2 + 4HF = SiF_4 + 2H_2O$; $SiF_4 + 4H_2O = 4HF + Si(OH)_4$ (or, $SiO_2.2H_2O$). [This reaction is used to detect silica or a silicate.] On heating silica with alkalis, silicates are formed : $SiO_2 + 2NaOH = Na_2SiO_3 + H_2O$. [This reaction indicates that SiO_2 is an acidic oxide.] Carbonates of alkali and alkaline earth metals also react with silica, when heated, to form the corresponding metal silicates, with the liberation of carbon dioxide : $CaCO_3 + SiO_2 = CaSiO_3 + CO_2$. At elevated temperatures, silica is reduced by carbon to silicon carbide, which decomposes at above 3000°C to form silicon and graphite : $SiO_2 + 3C = SiC + 2CO$; $SiC = Si + C$ (graphite). When an intimate mixture of SiO_2 and coke is heated to white-heat in a current of chlorine gas, silicon tetrachloride is formed : $SiO_2 + 2C + 2Cl_2 = SiCl_4 + 2CO$. As silica is non-volatile, it displaces the anhydride of much stronger sulphuric acid from its salts at high temperatures : $Na_2SO_4 + SiO_2 = Na_2SiO_3 + SO_3$.

Silica gel : On adding mineral acids to a concentrated solution of sodium silicate, a jelly of colloidal silicic acid (or hydrous silica) is obtained. On heating this gelatinous mass at 300°C under vacuum, a hard, transparent material is obtained.

This is disintegrated, washed with water and dried. The dried granules still contains about 5-6% moisture, and is known as **silica gel** ($SiO_2.nH_2O$).

Silica gel is used as a drying agent (for moisture), a decolorizing agent and as an absorbent. It is also used in petroleum industry for removing sulphur-compounds and also as a catalyst or a support for other catalysts.

Quartz glass or Silica glass : When sand or quartz is headed in an electric furnace (or in oxy-hydrogen flame) above 1710°C, it melts into a viscous, transparent, glassy mass, which solidifies to a glass-like mass on cooling. It is malleable and can be transformed into any desired shape. This is called **quartz glass or silica glass.** It has a sp. gr. of 2·2 and possesses certain properties which are much superior to those of ordinary glass. Thus, they are infusible upto 1000°C (ordinary glass melts at 500°–600°C), has a very low coefficient of thermal expansion, so that the hot articles made of them do not crack (like ordinary glass) when quenched in water ; it is transparent to visible light, infra-red and ultra-violet radiations (ordinary glass is opaque to ultra-violet radiations) ; it is free from alkali and is not attacked by acids (except HF). For these qualities, silica glass is much used for the preparation of crucibles, basins, combustion tubes, threads and many other laboratory apparatus, lenses, prisms *etc.* Translucent silica glass is known as **vitreosil.**

Uses of Silica : Sand is used in the manufacture of glass, porcelain and for making sand-paper and mortar. Silica glass is used for making laboratory apparatus, combustion tubes, silica threads, lens, prisms *etc.* Silica gel is used as a drying agent, absorbent *etc.* Silica bricks are used as furnace-lining. Sandstone is used as a building material.

Silicon Halides : Silicon dihalides are not formed. Silicon tetrahalides, SiX_4, (X = F, Cl, Br, I) are well-known, and they are all tetrahedral and covalent compounds. Catenated halides (having Si-Si bonds in the molecules) of the composition Si_2X_6 are formed by F_2, Cl_2, Br_2 and I_2 ; but with Cl_2, higher homologues upto Si_6Cl_{14} have also been isolated. Besides, a number of mixed halides like SiF_3I, $SiCl_2Br_2$, $SiFCl_2Br$ (except SiFClBrI, which is the interesting ultimate product) and some oxy-halides of the composition $Cl_3SiO(SiCl_2O)_nSiCl_3$ ($n = \sim 4$) have been prepared.

Silicon tetrafluorde (SiF_4) is generally prepared by heating barium silicofluoride ($BaSiF_6$) alone, or a mixture of metallic fluoride, silica and conc. sulphuric acid : $BaSiF_6 = BaF_2 + SiF_4$; $2CaF_2 + SiO_2 + 2H_2SO_4 = 2CaSO_4 + SiF_4 + 2H_2O$. In the latter case, the evolved gas is passed through dry sodium fluoride to remove HF, and then collected over mercury.

It is a colourless, fuming and non-combustible gas. It does not support the combustion of a burning taper ; but, heated sodium and potassium burn in the gas : $2SiF_4+4K=K_2SiF_6+2KF+Si$. It reacts with the oxides of calcium and barium to form silica and the fluoride of the corresponding metal : $2CaO+SiF_4=SiO_2+2CaF_2$. It is rapidly hydrolysed by water to give silicic acid : $SiF_4+4H_2O=Si(OH)_4+4KF$. [A secondary reaction between the unchanged SiF_4 and the HF generated, produces hydrofluosilicic acid : $SiF_4+2HF=H_2SiF_6$.] Analogously, the hydrolysis by alkalis produces silicate, fluoride and water : $SiF_4+8\ OH^-=SiO_4^{4-}+4F^-+4H_2O$.

Silicon tetrachloride ($SiCl_4$) is obtained as a colourless fuming liquid by passing dry Cl_2 over heated amorphous silicon, or better over an intimate mixture of silica and powdered coke, strongly heated in a porcelain tube : $Si+2Cl_2=SiCl_4$; $SiO_2+2C+2Cl_2=SiCl_4+2CO$. Silicon tetrachloride vapours are condensed in a freezing mixture and the resultant liquid is distilled over mercury to remove excess chlorine, and then stored in sealed tubes.

Silicon tetrachloride is a colourless, fuming liquid (b.p.=58°C). It is readily hydrolysed by water : $SiCl_4+2H_2O=Si(OH)_4+4HCl$. Together with ammonia, silicon tetrachloride is used to produce smoke-screen in war.

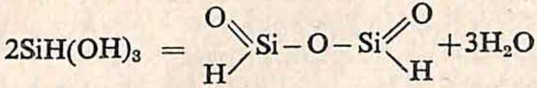
Silicon tetrabromide ($SiBr_4$) is a liquid (m.p. 5·2°C ; b.p. 153°C) which is formed by heating amorphous silicon in bromine-vapours. **Silicon tetraiodide (SiI_4)** is a solid, and is similarly obtained on heating silicon in vapours of iodine.

Disilicon hexachloride (Si_2Cl_6) is formed along with $SilC_4$ and Si_3Cl_8, when silicon is heated in a stream of dry Cl_2, and is separated as a colourless, fuming liquid by fractionation. The reaction between Si_2I_6 and Cl_2 also gives Si_2Cl_6. The vapours of the hexachloride ignites on heating in air. It is hydrolysed by water to form silico-oxalic acid : $Si_2Cl_6+4H_2O=(SiOOH)_2+6HCl$. The product is decomposed into sodium silicate and hydrogen, on treatment with alkali : $(SiOOH)_2+4NaOH=2Na_2SiO_3+2H_2O+H_2$.

Halogeno-silanes : The replacement of hydrogen atom(s) of a silane by halogens gives halogeno-silanes, and they are analogous to the corresponding halogen-derivatives of hydrocarbons. Among the halogeno-silanes, the most important is $SiHF_3$, $SiHCl_3$, $SiHBr_3$ and $SiHI_3$, which are commonly known as silico-fluoroform, silico-chloroform, silico-bromoform and silico-iodoform respectively.

Silico-chloroform ($SiHCl_3$) is obtained as a colourless, fuming liquid (b.p.=35°C), on passing dry hydrogen chloride gas over silicon, heated to dull red heat : $Si+3HCl=SiHCl_3+H_2$. The vapours are condensed into a liquid by a freezing mixture and the liquid is fractionated to separate $SiHCl_3$ from $SiCl_4$ which is also formed during the reaction. It is a highly inflammable liquid which burns with a green-edged flame to form white fumes of finely divided silica. It decomposes at about 800°C to give silicon, silicon tetrachloride and hydrogen : $4SiHCl_3 = Si + 3SiCl_4 + 2H_2$. Silicochloroform is much more reactive than chloroform, and is readily hydrolysed by water to form *ortho-silicoformic acid* [$SiH(OH)_3$], which, being unstable, readily loses water to form the *anhydride of silico-formic acid* ($H_2Si_2O_3$) :

$$SiHCl_3 + 3H_2O = SiH(OH)_3 + 3HCl\ ;$$



$$2SiH(OH)_3 = \overset{O}{\underset{H}{>}}Si-O-Si\overset{O}{\underset{H}{<}} + 3H_2O$$

Silicofluoroform ($SiHF_3$) is a combustible gas, and is obtained by the action of stannic fluoride on silico-chloroform : $4SiHCl_3 + 3SnF_4 = 4SiHF_3 + 3SnCl_4$.

Silicobromoform ($SiHBr_3$), a liquid boiling at 110°C, and silicoiodoform ($SiHI_3$), a red liquid boiling at 220°C are prepared by heating silicon in HBr and HI. Their reactions are similar to those of silico-chloroform.

Hydrofluosilicic acid or fluosilicic acid (H_2SiF_6) : Although the pure, anhydrous H_2SiF_6 cannot be prepared, an aqueous solution of the acid is made by passing SiF_4 into water : $3SiF_4 + 4H_2O = Si(OH)_4 + 2H_2SiF_6$. The gelatinous precipitate of silicic acid is filtered off. It is prepared on a large scale by dissolving silica in aqueous hydrofluoric acid : $SiO_2 + 6HF = H_2SiF_6 + 2H_2O$. It is also obtained as a by-product in the manufacture of superphosphate of lime.

Hydrofluosilicic acid is a strong acid (as strong as H_2SO_4) and can be titrated with caustic alkalis. The concentrated aqueous solution of the acid is a fuming, colourless liquid which decomposes into SiF_4 and HF on heating. Pure H_2SiF_6 does not corrode glass ; but, on evaporation, the acid partially decomposes to give hydrofluoric acid which corrodes glass. It reacts with alkalis to form alkali fluosilicates or silicofluorides which are decomposed by excess of alkali into alkali fluoride, silica and water : $H_2SiF_6 + 2NaOH = Na_2SiF_6 + 2H_2O$; $Na_2SiF_6 + 4NaOH = 6NaF + SiO_2 + 2H_2O$. Of the many known metal-fluosilicates, the majority are extremely soluble in water, notable exceptions being those of the alkali metals, barium, yittrium and the lanthanides. The fluosilicates are decomposed on heating or on treatment with conc. sulphuric acid : $Na_2SiF_6 = SiF_4 + 2NaF$; $Na_2SiF_6 + H_2SO_4 = Na_2SO_4 + SiF_4 + 2HF$.

Fluosilicates are useful as insecticides. Magnesium fluosilicate solution is used to harden and polish concrete surfaces. Many heavy metal fluosilicates are used in the electrodeposition of the metals (*e.g.* lead). Hydrofluosilicic acid is used as a reagent for the detection and estimation of potassium.

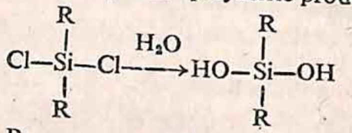
Silicones : The silicones are polymeric organo-silicon compounds, containing Si—O—Si linkages, and are built up of alkyl- or aryl-substituted siloxane groups. The starting materials for the manufacture of silicones are alkyl or aryl substituted chlorosilanes which are prepared by the Grignard reaction.

$$SiCl_4 + CH_3MgCl \rightarrow CH_3.SiCl_3 + MgCl_2 \;;$$
$$CH_3.SiCl_3 + CH_3MgCl \rightarrow (CH_3)_2SiCl_2 + MgCl_2,$$

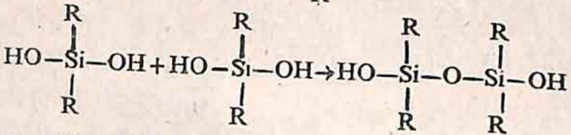
or by the direct chlorination of silicon by alkyl chlorides is presence of copper catalyst.

$$Si + 2CH_3Cl \xrightarrow{Cu} (CH_3)_2SiCl_2.$$

The hydrolysis of dialkyldichlorosilanes forms *silanols* as intermedtates, which condense subsequently to give the polymeric products.

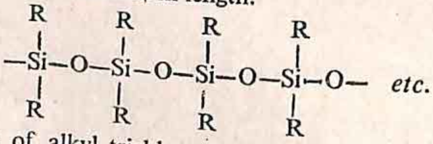


$$Cl{-}\underset{R}{\overset{R}{Si}}{-}Cl \xrightarrow{H_2O} HO{-}\underset{R}{\overset{R}{Si}}{-}OH$$



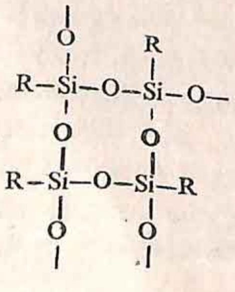
$$HO{-}\underset{R}{\overset{R}{Si}}{-}OH + HO{-}\underset{R}{\overset{R}{Si}}{-}OH \rightarrow HO{-}\underset{R}{\overset{R}{Si}}{-}O{-}\underset{R}{\overset{R}{Si}}{-}OH$$

Since an active OH group is left at each end of the chain, polymerisation continues and the chain increases in length.



$$-\underset{R}{\overset{R}{Si}}{-}O{-}\underset{R}{\overset{R}{Si}}{-}O{-}\underset{R}{\overset{R}{Si}}{-}O{-}\underset{R}{\overset{R}{Si}}{-}O- \quad etc.$$

The hydrolysis of alkyl trichlorosilane ($RSiCl_3$) gives very complex cross-linked polymers of the type,



By controlled mixing of the reactants, the hydrolysis produces any desired type of the above polymers. The extent of cross-linking and the nature of the R group determine the properties of the polymers. Materials ranging from oils (which remain fluid at very low temperature) to rubber-like solids are known for straight-chain polymers of two to several thousand units, their boiling points and viscosity increasing with the chain length. Most of the polymers are water-repellant, heat-stable, have high dielectric constants and resistant to oxidation and attack by many organic reagents. On strong heating (~ 400°C) in air, silicones with straight chains are rapidly oxidised and cross-links are formed, with the result that the polymers become brittle, and crack to produce materials of low molecular weight or those with cyclic structures. On strong heating in absence of air, silicones soften and form volatile products, but oxidation and cross-linking do not take place.

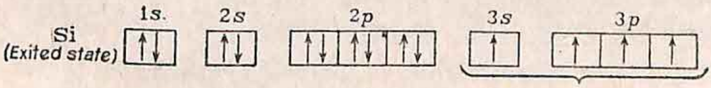
Silicones are used as water-proofing and anti-foaming agents, as lubricants and polishes, in cosmetics *etc*. Silcone rubbers are useful since they retain their elasticity from −90°C to +250°C and because of their good electrical insulating property. Silicone resins are used in paints and varnishes.

Silicic acids and Silicates.

Two principal silicic acids are known. These are (i) **Orthosilicic acid (H_4SiO_4)** and **metasilicic acid (H_2SiO_3).**

(i) **Orthosilicic acid** is formed as a white gelatinous precipitate on passing silicon tetrafluoride or tetrachloride vapours into water : $SiF_4+4H_2O=H_4SiO_4+4HF$. The precipitate is filtered, washed successively with water and ether, and dried by pressing between folds of blotting paper, when amporphous white powder of H_2SiO_4 is obtained.

Orthosilicic acid behaves as an extremely weak tetrabasic acid and forms metal salts (orthosilicates) which contain discrete SiO_4^{4-} groups. The electronegativity difference between O and Si (3·5−1·8=1·7) suggests that the Si−O bonds in SiO_4^{4-} are covalent with large ionic character. The radius-ratio $Si^{+4} : O^{2-}$ being 0·29, Si in SiO_4^{4-} is 4-coordinate and tetrahedral, which also follows from the hybridization of the orbitals used in bonding, as shown below :



4 unpaired electrons form four sp^3 hydrid bonds (tetrahedral).

Esters of orthosilicic acid with alcohols and phenols are also known. Methyl and ethyl esters of orthosilicic acid, $(CH_3)_4 SiO_4$

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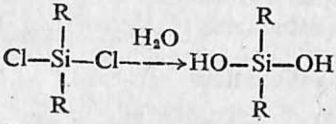
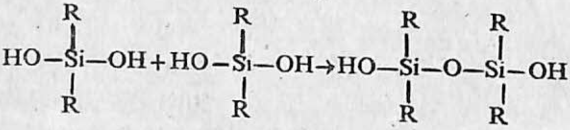


$$Cl-\underset{R}{\overset{R}{Si}}-Cl\xrightarrow{H_2O}HO-\underset{R}{\overset{R}{Si}}-OH$$



$$HO-\underset{R}{\overset{R}{Si}}-OH+HO-\underset{R}{\overset{R}{Si}}-OH\rightarrow HO-\underset{R}{\overset{R}{Si}}-O-\underset{R}{\overset{R}{Si}}-OH$$

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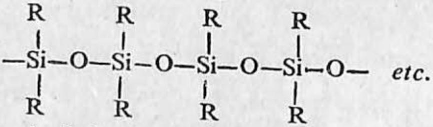

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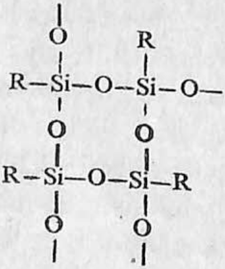

$$\begin{array}{c}
\begin{array}{ccccc} & | & & & \\ & O & & R & \\ & | & & | & \\ R- & Si & -O- & Si & -O- \\ & | & & | & \\ & O & & O & \\ & | & & | & \\ R- & Si & -O- & Si & -R \\ & | & & | & \\ & O & & O & \\ & | & & | & \end{array}
\end{array}$$

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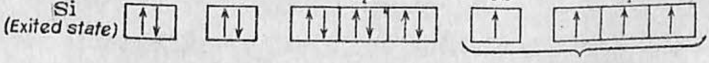


4 unpaired electrons form four sp^3 hydrid bonds (tetrahedral).

Esters of orthosilicic acid with alcohols and phenols are also known. Methyl and ethyl esters of orthosilicic acid, $(CH_3)_4$ SiO_4

and $(C_2H_5)_4SiO_4$ respectively, are prepared by the reaction between $SiCl_4$ and dry CH_3OH and C_2H_5OH.

(ii) **Metasilicic acid** is prepared by adding hydrochloric acid to a concentrated solution of sodium silicate, and dehydrating the resultant gelatinous precipitate with 90% alcohol : $Na_2SiO_3+2HCl=2NaCl+H_2SiO_3$. It forms white amorphous powder and is a very weak acid.

Dehydration of orthosilicic produces successively metasilicic acid (H_2SiO_3), disilicic acid ($H_2Si_2O_5$) and trisilicic acid ($H_2Si_3O_8$).

Metal silicates are obtained by melting silica with basic oxides. The salts of acids, which are volatilised on heating, can also be used in place of basic oxides. Under such conditions, silica unites with varied proportions of the oxides to form well-defined salts (silicates). The *ortho* and *meta* silicates are produced by the union of silica and the metal oxide in the proportions shown by the following equations :

$$SiO_2+2M^I{}_2O=\underset{\text{orthosilicate}}{M^I{}_4SiO_4}, \text{ and } SiO_2+M^I{}_2O=\underset{\text{metasilicate.}}{M^I{}_2SiO_3}$$

Silicates containing 2, 3 *etc*. molecular proportions of SiO_2 per $M^I{}_2O$ are called *disilicate*, *trisilicate etc*. They are sometimes called, in general, *polysilicates*.

The alkali-metal silicates are soluble in water, the aqueous solutions being strongly alkaline due to hydrolysis : $2Na_2SiO_3+H_2O=N_2Si_2O_5+2NaOH$. Some metallic silicates, which are insoluble in water, dissolve in strong acids, with the separation of gelatinous silica. Many silicates, however, are not decomposed even by strong acids (other than HF, which attacks them and forms SiF_4). But, the insoluble silicates may be decomposed by fusing with alkali carbonates : $MgSiO_3+Na_2CO_3=MgCO_3+Na_2SiO_3$.

Silicates occur in many important minerals like **felspar (orthoclase), $KAlSi_3O_8$** ; **Kaolin (china clay), $H_2Al_2(SiO_4)_2 \cdot 2H_2O$** ; **Mica, $KHMg_2Al_2(SiO_4)_3$ and $KH_2Al_3(SiO_4)_3$** ; **Asbestos, $Mg_3Ca(SiO_3)_4$** ; **Talc (Soap stone), $H_2Mg_3(SiO_3)_4$** ; **Beryl, $Be_3Al_2(SiO_3)_6$** ; **Garnet, $Ca_3Al_2(SiO_4)_3$** *etc*. Silicates of zinc, beryllium and cadmium are used as inside-coating of fluorescent lights.

Sodium silicate (Na_2SiO_3) is prepared by melting pure sand and sodium carbonate, or by the reaction of freshly precipitated hydrated silica with the calculated amount of caustic soda : $SiO_2+Na_2CO_3=Na_2SiO_3+CO_2$; $SiO_2+2NaOH=Na_2SiO_3+H_2O$. [On a commercial scale, sodium silicate is prepared by melting sand with sodium sulphate and coke.] The product solidifies from the melt (m.p. = 1088°C) and the solid mass is broken into lumps. It is generally grey or greenish in colour due the presence of traces of iron as impurity. Sodium silicate is commonly sold in the market in the form of thick aqueous solution (*water glass*) which is prepared by treating the solid with steam, or heating it with water under pressure in an autoclave. Sodium silicate crystallises as a hydrate from aqueous solution. Hydrated sodium silicate comes into commerce under the name of *alkasil*. The aqueous solution of sodium silicate is alkaline due to hydrolysis.

The thick, transparent aqueous solution of sodium or potassium silicate is commercially known as *water glass*. [Potassium silicate is prepared by melting sand and potash.] Water glass solutions are used for impregnating fabric during calico-printing, for sizing paper, for stiffening bandages for fractures of the bones, for preparing adhesives, for affixing labels to glass, for fire-proofing wood and textiles and for the preservation of eggs (4 – 10% solutions are used). Powdered water glass gel is used as a filler in soaps.

Classification of silicates : A common way of classifying silicates is based on their structures which are often complex. This classification depends on the manner in which the $(SiO_4)^{4-}$ tetrahedra (Fig- 15-7) are linked together in the material.

(i) **Orthosilicates :** These materials always contain discrete $(SiO_4)^{4-}$ tetrahedra arranged in parallel rows, and the associated metal ions lie within the intermediate holes. The oxygen atoms form coordinate bonds to the metal ions, and according to the coordination number of the metal, various structures become possible. Thus, in Zn_2SiO_4 (*Willemite*) and Be_2SiO_4 (*Phenacite*), the metal ions are tetrahedrally surrounded by four oxygen atoms, whereas in Mg_2SiO_4 (*Forsterite*) and $ZrSiO_4$ (*Zircon*), the metal ions are surrounded by six and eight oxygen atoms respectively.

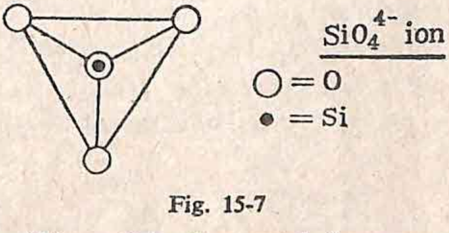


Fig. 15-7

(ii) **Pyrosilicates :** The simplest, although uncommon, condensed silicate ion is present in the pyrosilicates such as $Sc_2(Si_2O_7)$, in which two tetrahedral $(SiO_4)^{4-}$ units are joined by showing one oxygen, producing the $(Si_2O_7)^{6-}$ ions (fig. 15-8).

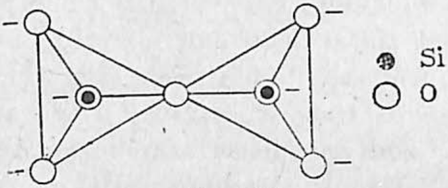


Fig. 15-8

(iii) **Cyclic silicates :** Sharing of two oxygens per tetrahedron gives rise to ring or cyclic structures of the silicates, and the

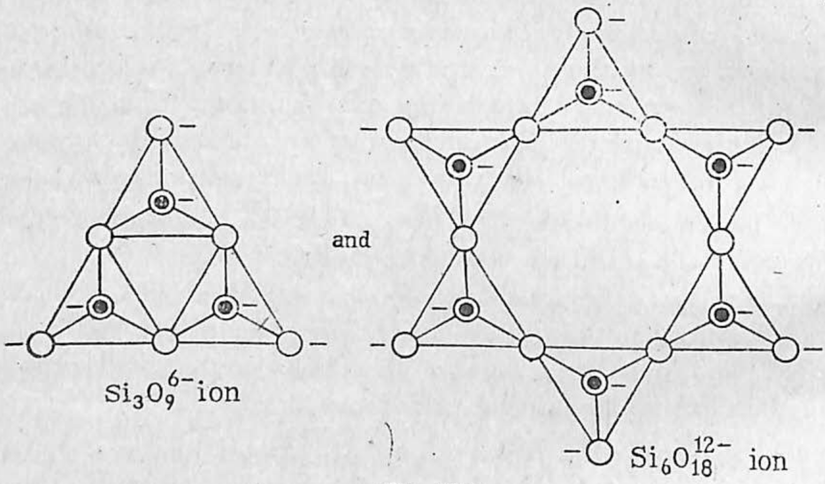
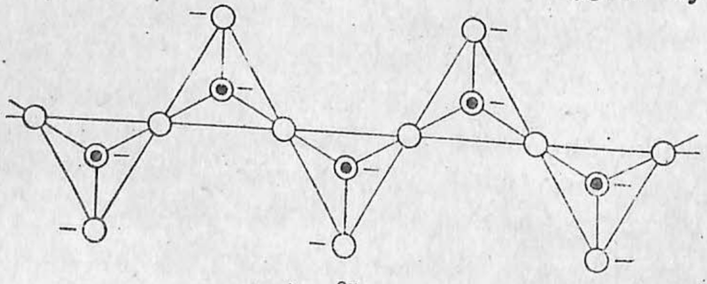


Fig. 15-9

condensed silicate ion produced has the general formula $(SiO_3)_n^{2n-}$. Minerals like *beryl* $[Be_3Al_2(Si_6O_{18})]$ and *wallostonite* $[Ca_3(Si_3O_9)]$ have such cyclic structure.

(iv) **Chain silicates :** Sharing of two oxygens by each



$(SiO_3)_n^{2n-}$ chain

tetrahedron may also result in simple chains of silicate ions having the formula $(SiO_3)_n{}^{2n-}$, as in *spodumene* [$LiAl(SiO_3)_2$]. Double chains of formula $(Si_4O_{11})^{6n-}$, where two simple chains are joined together by shared oxygens (some tetrahedra share two oxygens and others three) are also known.

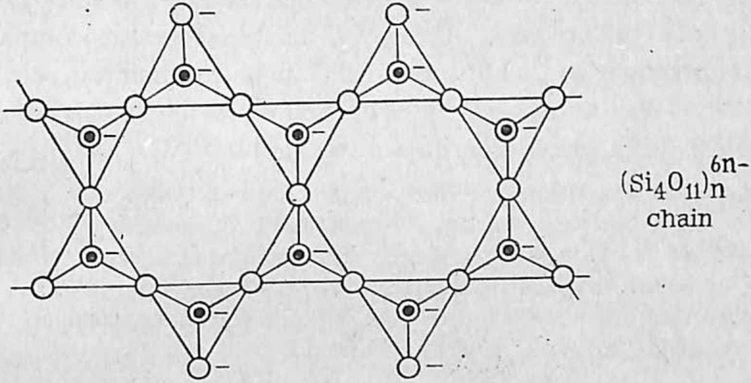


Fig. 15·11

(v) **Sheet silicates :** When three oxygens per tetrahedron are shared, an infinite two-dimensional sheets of formula $(Si_2O_5)_n{}^{2n-}$ are formed, as in mica. The individual layers of these sheets are

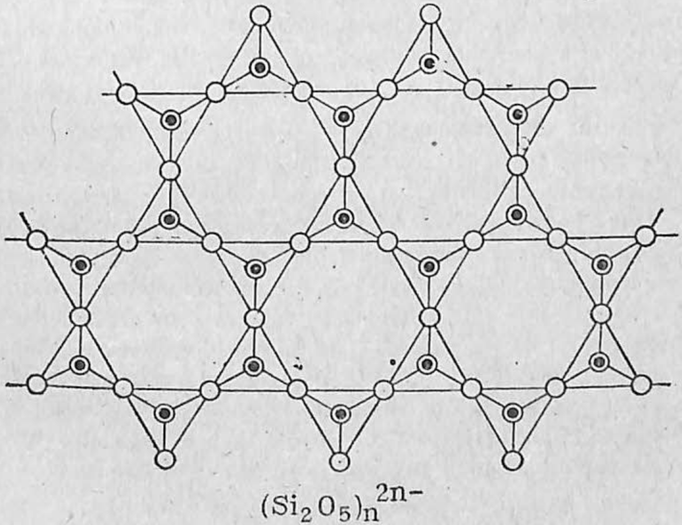


Fig. 15·12

held together by weak electrostatic attraction of the associated metal ions and hence, they cleave into thin sheets on slight deformation.

(vi) **Three-dimensional silicates :** When all the four oxygen atoms of a SiO_4 -tetrahedron are shared by other tetrahedra, a three-dimensional lattice is formed. The simplest example is silica (SiO_2). Isomorphous replacement of Si by Al in the lattice is accompanied by the presence of additional metal ions to maintain electro-neutrality. Well-known examples of such three-dimensional silicates are zeolites, ultramarine *etc.* [See also chapter XIV].

Tests of Silica and silicates : When silica or a silicate is heated with a fluoride and conc. H_2SO_4, and the issuing gas is brought in contact with water, a white gelatinous precipitate of silicic acid is formed. They are quantitatively estimated by weighing as SiO_2 after digestion and repeated evaporation with acids, or by a determining the loss in weight after strongly heating with hydrofluoric acid in platinum crucible (*i.e.* by volatilizing Si as H_2SiF_6).

Other compounds of silicon.

Silicides : These are binary compounds of silicon with the more electropositive elements (mainly metals) and are prepared either by melting the two components together or by reducing SiO_2 with excess of the metal concerned. Most of the metal silicides have metallic appearance and resemble inter-metallic compounds. Except the alkaline earth silicides and lithium silicide (the only alkali silicide known), the other silicides are stable towards water and dilute acid (the former silicides are decomposed by water and dil. acids). Majority of the silicides possess compositions which do not tally with the normal valence states of the components. Many silicides, *e.g.* those of Mg and Mn, are decomposed by acids to give silicon hydrides and hydrogen.

Silicon carbide or carborundum (SiC) : The substance is manufactured by heating a mixture of sand and crushed coke (along with some common salt and saw-dust) in an electric furnace at about 2000°C (*Acheson process* ; see page 14) : $SiO_2+3C=SiC+2CO\uparrow$. [The temperature should not exceed 2200°C, as SiC decomposes above this temperature into silicon and graphite.] Pure silicon carbide is a colourless solid (density=3·2), but the commercial variety is dark coloured due to impurities. It is almost as hard as diamond and has a crystal structure similar to that of the latter. It is extremely resistant to chemical attack even at high temperatures. [It is, however, decomposed by molten caustic alkalis in presence of air and is completely oxidised by red-hot dichormate : $SiC+4KOH+2O_2=K_2SiO_3+K_2CO_3+2H_2O$.] Silicon carbide is used as a valuable abrasive and also for making refractory bricks. [See also page 43 of this Vol.]

Silicon sulphide (SiS_2) is obtained by melting amorphous silicon with a three-fold excess of sulphur. The product is purified by sublimation under reduced pressure, when colourless, silky, feather-like crystals are formed. It is stable in dry air, but is hydrolysed by water : $SiS_2+2H_2O=SiO_2+2H_2S$. The crystals of SiS_2 have been found to be built up of infinite chain as shown below, in which each Si-atom is tetrahedrally surrounded by 4 S-atoms and each S-atom is joined to 2 Si -atoms.

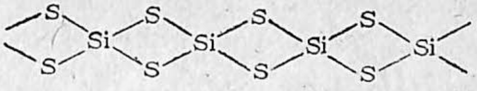


Fig. 15·13

Cationic silicon : The considerably high electronegative character of silicon debars it from existing as a stable cation, but complex species containing cationic silicon do exist. The reaction of silicon tetrachloride with acetylacetone (and probably with other β-diketones) in dry chloroform yields solid silicon tris-acetylacetone cation, in which 3 acetylacetone anions are combined with a hexacovalent, silicon to form an octahedral complex, $[Si(acac)_3]^+$. A number of salts, such as chloride, chloroaurate *etc.* of the complex cation has been described. The compounds are optically active and the *dextro* and *laevo* optical forms have been actually separated. [See fig. 7.19 at p. 305 ; Vol. I.]

Glass.

Although considered earlier as a *super-cooled liquid*, glass is now recognised as a completely vitrified (amorphous) solid which is a complex mixture of mainly alkali silicates (sodium and/or potassium silicate) and calcium silicate. It is generally obtained as a transparent material, either colourless or coloured, although translucent or opaque glass is also available. Glass is formed by melting silica (or quartz) with $CaCO_3$ and sodium carbonate (or potassium carbonate). It has no fixed and definite stoichiometry, but may be denoted by the approximate composition, X_2SiO_3, YCO_3, $6SiO_2$, where X=Na or K, Y=Ca. In some types of glass, a portion of SiO_2 may be substituted by B_2O_3 (borosilicate glass), and PbO, BaO, MgO, ZnO *etc.* may often be added to prepare glass with some special properties.

Glass is, therefore, a complex mixture of sodium (and/or potassium) silicate with alkaline earth (or some other heavy metal) silicates, which is formed as a more or less transparent and completely vitrified mass, when the melt of the above mixture is solidified.

Glass has found many useful applications due to some of its specialised properties. It is generally transparent (colourless or coloured) and becomes soft and plastic on heating to allow fabrication of articles of desired size and shape by blowing and moulding, or it can be rolled into sheets of different thicknesses. The softened glass becomes hard solid on cooling, without crystallisation. It is quite heat-resistant. It is not attacked by acids (except HF), but is corroded only very slowly by alkalis. These qualities of glass make it very suitable for preparing laboratory wares and bottles. It is completely *isotropic,* i.e., it exhibits similar properties in all directions. Glass is a bad conductor of heat, which results in the cracking of glass articles due to abrupt changes of temperatures.

According to its composition, glass is generally classified as follows :

(i) *Soft glass or Soda glass* : This type of glass contains sodium silicate and calcium silicate, along with silica. It can be melted at a comparatively lower temperature than the other types of glass. It is generally used for making ordinary cheap bottles, tubes and other glass vessels, glass panes for windows *etc.*

(ii) *Hard glass* (*Potash glass*) or *Bohemian glass* : When sodium silicate in the composition of soft glass is replaced by potassium silicate, hard or Bohemian glass is obtained. This type of glass is much harder and more resistant to chemical attack than the ordinary soft glass and melts at relatively higher temperatures. These qualities of this glass make it useful for fabricating chemical apparatus and combustion tubes.

(iii) *Flint glass or Lead glass* : Replacement of calcium silicate of hard glass by lead silicate produces *Flint glass* or *lead glass.* This type of glass has low melting point and comparatively lower resistance towards chemical attack ; but it has higher specific gravity and refractive index. [A particular variety of this glass, containing larger amounts of lead silicate, is known as *strass,* whose refractive index is as high as that of diamond.] Flint glass is largely used in many optical instruments and in preparing decorative articles of *cut glass.*

(iv) *Crown glass* : This type of glass is generally used in optical instruments, and it contains larger proportions of P_2O_5, along with potassium silicate and barium silicate.

(v) *Borosilicate glass* : Certain varieties of glass contain some proportion of Al_2O_3, B_2O_3, ZnO and BaO, along with P_2O_5. These are grouped together as *borosilicate glass* and are sold under the commerical names *Pyrex glass, Jena glass etc*. These are more resistant to heat and chemical attack and are less fragile. Their low thermal expansion makes them particularly suitable for making glass apparatus and vessels. These are used for making apparatus like beakers, flasks *etc*. Borosilicate glass, containing CdO, CdF_2 and high proportions of lead, are generally used in radiation work as protective glass.

Manufacture of glass : The raw materials required for the manufacture of glass are silica or quartz, calcium carbonate (in the form of chalk or marble) and calcined soda (or a mixture of sodium sulphate and powdered coke). For the preparation of potash glass (hard glass) and lead glass, sodium carbonate is replaced by K_2CO_3, and calcium carbonate is replaced (partly) by litharge (PbO) or white lead. Other additions like B_2O_3, Al_2O_3, P_2O_5 *etc*. are made in suitable amounts to obtain products of required specifications. The mixture of necessary amounts of the ingredients is melted with varying amounts of *cullet* (crushed waste glass from rejected glass articles or their trimmings) in the hearth of a tank furnace made of firebricks and heated by producer gas. [The ingredients generally contain certain impurities (such as iron oxide), which impart some greenish tinge to the melt. In order to remove this colour, KNO_3 or MnO_2 is added to the melt. The whole amount of the charge is not transferred into the furnace at a time for melting ; instead, a small portion of the mixture is added to cullet and heated to melting. When a melt is formed, further quantities of the mixture are added portion-wise to the melt. The cullet helps in melting the mixture.] The heating is carried out in a *regenerative method* (to minimize the wastage of heat) by alternating the directions of flow of the incoming fuel and that of the exit of the waste gas, so that the incoming producer gas is pre-heated before burning. The temperature of the furnace rises to about 1400°C and the charge melts into of copper and iron and also wolframite or ferrous tungstate, $FeWO_4$. So, the preliminary *concentration* of the ore is necessary, which is effected by washing the finely crushed ore in a flow of water. The lighter paticles of earthy or siliceous matter are carried away by the flow of water and the heavier particles of SnO_2 settle down. The concentrated ore is *roasted* in a reverberatory furnace, when the sulphides and aresenides are oxidised into volatile SO_2 and As_2O_3 which escape, and the copper and iron sulphides are converted into their oxides and sulphates. The roasted mass is first leached with water to remove the sulphates and then with dil. HCl which removes most of the oxides. The residue left behind after the acid-treatment contains SnO_2, along with some amount of the oxides of iron and tungsten. The dried residue is then subjected to *electromagnetic separation* (See vol. I, p. 365), when oxides of iron and tungsten are separated from SnO_2 which is about 75% pure and is known as *black tin*. *Reduction* of the enriched SnO_2 is then effected by mixing it with powdered coke and heating in reverberatory furnace (or a blast furnace) at about 1200°C. Tin dioxide is reduced by coke to metallic tin which melts at the temperature of the furnace and forms a lower molten layer below the slag. The molten layer is removed and cast into ingots : $SnO_2+2C=Sn+2CO$. The slag is generally rich in tin and the metal is subsequently recoverd from it.

The crude metal obtained in the above process is highly contaminated with iron and, to a lesser extent, with other metals. It is purified by re-melting on the inclined hearth of a reverberatory furnace (*liquation*), when molten tin flows out, leaving behind relatively infusible iron. The molten mass is then 'poled' with a billet of fresh green wood and vigorously stirred, when the other metals (along with some tin) are oxidised and collected as the oxide scum on the surface of the liquid metal and are removed. The metal obtained in this procedure is about 99% pure. Further purification may be made by electrolysis, using an acidified solution of stannous sulphate or fluosilicate, with impure tin blocks as anode and pure tin strips as cathode.

Recovery of tin from the slag is effected either by melting it with limestone and coke in a reverberatory furnace, or by fusion with scrap iron and coke :

$$SnSiO_3+CaO+C=Sn+CaSiO_3+CO\ ;$$

$$SnSiO_3+Fe=Sn+FeSiO_3\ ;\ SnO_2+2C=Sn+2CO.$$

Recovery of tin from tin-plated iron scraps: Much tin is recovered from scraps by electrolysis in caustic soda solution, where the scraps (in iron-wire basket) are made the anode. As tin is more readily acted upon than iron by chlorine gas *de-tinning* of tin-plated scraps by chlorination is also resorted to for its recovery from such scraps.

Properties : A lustrous, soft and silver-white metal (m.p. 231·8°C, density=7·28), tin can be rolled out into very thin sheets (*tin foils*). When a tin rod or sheet is bent, a creaking noise arises due to the friction of the crystallites one upon the other, and this is known as the '*cry of tin*'. The metal has three crystalline modifications, with the following equilibrium transition temperatures :

$$\underset{\text{'grey'}}{\alpha\text{-Sn}} \xrightleftharpoons{13{\cdot}2^\circ\text{C}} \underset{\text{'white'}}{\beta\text{-Sn}} \xrightleftharpoons{161^\circ\text{C}} \gamma\text{-Sn} \xrightleftharpoons{231{\cdot}8^\circ\text{C}} \text{Liquid Sn.}$$

α-Sn or grey in (density=5·75 at 20°C) is unstable above 13·2°C and is formed as a grey powder when white tin is cooled below the transition temperature. It has a diamond-type structure. Above 13·2°C, β-Sn or white tin exists, which is metallic in nature and contains distorted (tetragonal) close-packed arrangement of atoms in its crystals. Such an arrangement of atoms in the crystal-lattice accounts for its greater density (7·31 at 20°C). Above 161°C, white tin changes to the γ-Sn which is the rhombic modification and metallic in nature (density=9·56 at 20°C). It is very brittle and breaks into pieces when dropped from a little height and can be easily powdered. In very cold countries, tin plates swell and fall into powder due to the transformation into grey tin. This phenomenon is often known as '*plague of tin*'.

Tin is not affected by air or water at ordinary temperatures. But, at white heat, it is oxidised by air into tin dioxide. The vapours of the metal can be easily burned completely to the dioxide. Steam is decomposed by heated tin. It directly combines with chlorine and bromine at ordinary temperature, and with iodine on gentle warming, to form the corresponding tetrahalides. It also combines with sulphur on heating.

$$\text{Sn}+\text{O}_2=\text{SnO}_2\ ;\ \text{Sn}+2\text{H}_2\text{O (steam)}=\text{SnO}_2+2\text{H}_2\ ;$$

$$\text{Sn}+2\text{Cl}_2=\text{SnCl}_4\ ;\ \text{Sn}+2\text{S}=\text{SnS}_2.$$

Tin reacts with dilute acids very slowly, but it reacts readily with hot and concentrated HCl or H_2SO_4 :

$$\text{Sn}+2\text{HCl}=\text{SnCl}_2+\text{H}_2\ ;\ \text{Sn}+2\text{H}_2\text{SO}_4=\text{SnSO}_4+\text{SO}_2+2\text{H}_2\text{O}.$$

Cold and dilute HNO_3 reacts with tin to form stannous nitrate and ammonium nitrate :

$$4\text{Sn}+10\text{HNO}_3=4\text{Sn(NO}_3)_2+\text{NH}_4\text{NO}_3+3\text{H}_2\text{O}.$$

dehydrated to SnO_2 on strong heating : $Sn(OH)_4 = SnO_2 + 2H_2O$. It is amphoteric in nature and dissolves in acids and alkalis to form stannic salts and alkali stannates respectively. It is partially dehydrated to form H_2SnO_3 (α-metastannic acid) on drying over conc. H_2SO_4.

Besides the so-called ortho-stannic acid (H_2SnO_4) and α-metastannic acid (H_2SnO_3), another stannic acid, known as β-metastannic acid (commonly called *metastannic* acid, $H_2Sn_5O_{11}.4H_2O$), is also available. [All these stannic acids are actually hydrous SnO_2 with varying amounts of adsorbed water and the two metastannic acids are often called the *α-oxide* and the β-oxide respectively.] The α-acid is generally obtained by the slow, low-temperature hydrolysis of Sn(IV) compounds, whereas the β-acid results from the high-temperature hydrolysis or by the action of nitric acid on metallic tin. The two modifications of the acids differ much in properties. Thus, the α-acid is readily soluble in acids and bases, while the β-variety is quite inert to these reagents. X-ray studies have, however, shown that both the varieties have the same crystal structure. The difference in reactivity has been suggested to be due to the difference in the particle sizes (α-acid consists of relatively smaller particles than the β-acid), the nature of the surfaces of the particles *etc*. Conc. HCl slowly acts upon the β-acid to form a product that gives a colloidal solution with water—the *aqueous solution* forming a gel on boiling. It also forms a colloidal solution on treatment with alkali solutions, but, it is not possible to isolate crystalline alkali salts from these *solutions*—amorphous substances corresponding to the composition of the alkali-salts of the α-acid are obtained on evaporating the alkaline solutions. Fusion of the β-acid with alkalis, however, yields alkali β-stannates.

Gels of stannic acid or tin dioxide are used in dyeing. Metastannic acid (β) is used in the phosphate separation in qualitative inorganic analysis.

Stannic fluoride or Tin tetrafluoride (SnF_4) is prepared by gently heating tin tetrachloride ($SnCl_4$) with an excess of anhydrous hydrofluoric acid, or by dissolving freshly prepared SnO_2 in hydrofluoric acid. It forms colourless crystals (density= 4·78) which dissolve in water with the evolution of a large amount of heat. Crystalline double fluorides or *fluorostannates* can readily be obtained on mixing solutions of SnF_4 and other metal fluorides (or ammonium fluoride) and crystallising the mixture.

Stannic chloride or Tin tetrachloride ($SnCl_4$) : The compound is prepared by passing a stream of dry chlorine gas over molten tin and purifying the product through distillation. It can also be prepared by heating a mixture of powdered tin and mercuric chloride, and condensing the volatile stannic chloride. It is manufactured chiefly by treating tin-plate scraps with chlorine gas.

Stannic chloride is a colourless liquid (density=2·23 ; b.p.=114°C) which fumes in air due to hydrolysis by atmospheric moisture. It dissolves phosphorus, sulphur, iodine. arsenic triiodide, antimony triiodide and tin tetraiodide. The compound dissolves in water with considerable evolution of heat. Depending upon the conditions, several hydrates with 3, 5 or 8 molecules of water of crystallisation may be isolated from the aqueous solution. The pentahydrate, $SnCl_4.5H_2O$, forms water soluble, white, opaque and deliquescent crystals (m.p.=60°C). [This hydrate was earlier known as the *butter of tin* which is used as a mordant in dyeing. But; this name is now obsolete.] The aqueous solution of tin tetrachloride undergoes slow and reversible hydrolysis, with the ultimate formation of SnO_2 (see also page 75), which often remains in solution in a colloidal form : $SnCl_4+2H_2O \rightleftharpoons SnO_2+4HCl$. The resultant HCl reacts to some extent with the undecomposed $SnCl_4$ to form hexachlorostannic acid, $H_2[SnCl_6]$. Hydrolysis of $SnCl_4$ is largely prevented by the addition of hydrochloric acid, and this is due, not only to the pushing of the reversible hydrolytic reaction backward, but also due to the formation of $H_2[SnCl_6]$. The hexachlorostannic acid can be isolated as the white, crystalline hexahydrate, $H_2[SnCl_6].6H_2O$, by passing HCl gas through a concentrated aqueous solution of $SnCl_4$. The crystalline salts of this acid, *e.g.* $M_2[SnCl_6]$, where M=alkali metal or NH_4^+ ions, are obtained by the combination of alkali metal chlorides or NH_4Cl respectively with $SnCl_4$. Ammonium chlorostannate, $(NH_4)_2[SnCl_6]$, generally known as the *pink salt*, forms colourless crystals, readily soluble in water, and it is used as a mordant in dyeing. Tin tetrachloride forms addition-compounds with many substances, such as NH_3, PH_3, $POCl_3$, NOCl, organic sulphides (R_2S) and ethers (R_2O).

Tin tetrachloride is used as a mordant in dyeing and for weighting silk. It is used as a catalyst in chlorination reactions and as a condensing agent in organic synthesis.

Stannic bromide or Tin tetrabromide ($SnBr_4$) is prepared as a white crystalline mass (density=3·35 ; m.p.=33°C ; b.p.=203°C) by the direct union of metallic tin and bromine. It is soluble in water, and the tetrahydrate, $SnBr_4.4H_2O$, can be crystallised out from the aqueous solution. Hexabromostannic acid, $H_2[SnBr_6].8H_2O$ and its salts (*bromostannates*) are known. The hydrated acid forms colourless deliquescent fine crystals.

Stannic iodide or Tin tetraiodide (SnI_4) is prepared by the action of iodine (dissolved in CS_2) on tin. It is also formed by the action of KI on a concentrated solution of $SnCl_4$. The substance forms yellow, highly refractive, octahedral crystals (density=4·46 ; m.p. 146°C), readily soluble in organic solvents and is readily hydrolysed in aqueous solution. Hexaiodostannic acid is not definitely known, but some of its alkali-metal salts have been prepared.

Stannic sulphide or Tin disulphide (SnS_2) is prepared by heating a mixture of tin foil, sulphur powder and ammonium chloride. It is also precipitated on passing H_2S gas through a dilute acidic solution of Sn(IV) salts, or by the acidification of thiostannate solutions : $Sn+4NH_4Cl=(NH_4)_2SnCl_4+H_2+2NH_3$; $2(NH_4)_2SnCl_4+2S=SnS_2+$ $(NH_4)_2SnCl_6+2NH_4Cl$; $H_2[SnCl_6]+H_2S=SnS_2+6HCl$; $(NH_4)_2SnS_3$ $+2HCl=SnS_2+2NH_4Cl+H_2S$. When prepared by the dry method, stannic sulphide forms golden yellow scales, and is known as *mosaic gold* which is used for bronzing. Mosaic gold is insoluble in HCl and HNO_3 separately, but dissolves in aqua regia and also in alkali solutions. The product obtained by the wet method is yellow in colour and it dissolves in moderately concentrated, warm hydrochloric acid : $SnS_2+4HCl\rightleftharpoons SnCl_4+2H_2S$. It also dissolves readily in solutions of alkali sulphides or colourless and yellow ammonium sulphide [NH_4HS and $(NH_4)_2S_x$ respectively] to form thiostannates. Solutions of caustic alkalis dissolve SnS_2, forming stannates and thiostannates. [It is, however, insoluble in ammonium carbonate solution.] All the above solutions give the yellow precipitate of SnS_2 on acidification :

$$SnS_2+NH_4HS+NH_3=(NH_4)_2\,SnS_3\,;$$
$$(NH_4)_2\,SnS_3+2HCl=SnS_2+2NH_4Cl+H_2S.$$
$$3SnS_2+6NaOH=Na_2SnO_3+2Na_2SnS_3+3H_2O\,;$$
$$Na_2SnO_3+2Na_2SnS_3+6HCl=3SnS_2+6NaCl+3H_2O.$$

[SnS_2 is not, however, precipitated by passing H_2S through a solution of stannic salt in presence of oxalic acid, because of the formation of stable complex species, $[Sn(C_2O_4)_4(H_2O)_2]^{4-}$, in solution. Separation of Sb and Sn in the qualitative analysis depends on such complex-formation.]

Stannic sulphate, [$Sn(SO_4)_2.2H_2O$], can be prepared as colourless needles on crystallising a solution of freshly precipitated hydrated tin dioxide in dilute sulphuric acid.

Stannous Compounds.

Stannous oxide (SnO) and Stannous hydroxide [$Sn(OH)_2$] : When a solution of a stannous salt is treated with a solution of an alkali carbonate or with a little alkali hydroxide solution, a sparingly soluble white precipitate is obtained. On careful drying, the product corresponds to the composition $Sn(OH)_2$, the so-called stannous hydroxide, which is often represented as the hydrated stannous oxide, $2SnO_2{\cdot}2H_2O$. On standing in contact with alkali or with the solution from which it is precipitated, it is readily transformed into the dark coloured anhydrous stannous oxide, SnO (the conversion is accelerated at elevated temperatures). Anhydrous stannous oxide may be prepared by rubbing stannous chloride with a small excess of Na_2CO_3 and heating the mixture on a sand-bath with constant stirring, till the mass turns black. The cooled mass is then leached with water, when finely divided blue-black SnO is obtained.

It may also be prepared by heating stannous oxalate in absence of air : $SnC_2O_4=SnO+CO+CO_2$.

Stannous oxide is oxidised to SnO_2 on heating in air (the oxidation begins below 300°C). Both SnO and $Sn(OH)_2$ are amphoteric in nature and dissolve in acids to form stannous salts and in alkali solutions to form stannites (stannous hydroxide forms hydroxostannites in addition) : $SnO+2HCl=SnCl_2+H_2O$; $Sn(OH)_2+2HCl=SnCl_2+2H_2O$; $SnO+2NaOH=Na_2SnO_2+H_2O$; $Sn(OH)_2 + 2NaOH = Na_2SnO_2 + 2H_2O$; $Sn(OH)_2 + NaOH= Na[Sn(OH)_3]$. A very strong solution of alkali reacts with SnO to form alkali stannate and spongy tin metal : $2SnO+2NaOH =Na_2SnO_3+Sn+H_2O$. Due to their relatively ready tendency to be transformed into the tetravalent tin compounds, stannous hydroxide and stannite solutions have strong reducing properties. Thus, a bismuth salt is reduced to metallic bismuth on treatment with an alkaline solution of stannite :

$2Bi(NO_3)_3+6NaOH+3Na_2SnO_2=2Bi+3Na_2SnO_3+6NaNO_3+3H_2O$.

Such reducing properties make them technically useful in vat-dyeing and dye-printing.

[**Stannous fluoride (SnF_2)** is prepared by evaporating SnO with hydrofluoric acid in absence of air. It forms colourless, water-soluble crystals.

Stannous chloride ($SnCl_2$) can be obtained in the anhydrous state by heating tin foils or granules in a current of dry hydrogen chloride gas. The hydrated salt, $SnCl_2.2H_2O$ is prepared by dissolving metallic tin in conc. hydrochloric acid, followed by crystallisation : $Sn+2HCl=SnCl_2+H_2$. The hydrated salt can be made anhydrous by heating in a current of dry hydrogen chloride.

Anhydrous stannous chloride is a lustrous white solid (density =3·95 ; m.p.=247°C). It is soluble in water and also in alcohol, acetone, ether, ethyl acetate *etc.* The dilute aqueous solution becomes turbid due to hydrolysis into basic salt : $SnCl_2+H_2O=Sn(OH)Cl+HCl$. Such hydrolysis can be prevented by the addition of hydrochloric acid to the aqueous solution. But, the acidic solution of $SnCl_2$ has a tendency to be oxidised to the stannic state, and as such, the acidic aqueous solution of $SnCl_2$ is preserved by adding some tin granules to the solution : $3SnCl_2+\frac{1}{2}O_2+H_2O=SnCl_4+2Sn(OH)Cl$. The hydrated stannous chloride forms white non-deliquescent crystalline (monoclinic or bipyramid) mass, with a density of 2·71 and melting at 40·5°C. Stannous chloride is a good reducing agent. It reduces silver and gold salts into the metallic state. Mercuric chloride is reduced to mercurous chloride and then to grey metallic mercury (if $SnCl_2$ is used in excess). It also reduces ferric salts to ferrous salts, cupric salts to cuprous salts, arsenates to arsenites. permanganates to manganous salts, chromates to chromic salts, organic nitro-compounds to amines and the diazonium salts to the hydrazine salts .

$2Ag^{+}+Sn^{+2}=2Ag\downarrow+Sn^{+4}$: $2AuCl_3+3SnCl_2=2Au\downarrow+3SnCl_4$; $2HgCl_2+SnCl_2=Hg_2Cl_2+SnCl_4$; $Hg_2Cl_2+SnCl_2=2Hg+SnCl_4$; $2FeCl_3+SnCl_2=2FeCl_2+SnCl_4$; $2CuCl_2+SnCl_2=Cu_2Cl_2+SnCl_4$; $K_2Cr_2O_7+14HCl+3SnCl_2=3SnCl_4+2KCl+2CrCl_3+7H_2O$.

Stannous chloride reacts with iodine solution to form $SnCl_2I_2$, and this reaction is used in the iodimetric estimation of tin : $SnCl_2+I_2=SnCl_2I_2$. Crystals of *chlorostannous acid*, $HSnCl_3.\ 3H_2O$, are obtained by freezing at −27°C a solution of $SnCl_2$ in conc. HCl. Crystalline chlorostannites of the alkali metals of the composition $MSnCl_3$ and M_2SnCl_4 have also been isolated. Dry $SnCl_2$ adds on a molecule of NH_3 when it is warmed in a stream of the dry gas.

Stannous chloride is used as a reducing agent in qualitative and quantitative analysis. In the industry, the salt finds application as a reducing agent for nitro-, azo- and diazonium compounds and also as a mordant in dye-printing as also for preparing lake-colours.

Stannous bromide ($SnBr_2$) is obtained as a pale yellow mass (density=4·92; m.p.=232°C) by the action of hydrobromic acid on metallic tin. Distillation of metallic tin with $HgBr_2$ also produces $SnBr_2$.

Stannous iodide (SnI_2) is obtained as a yellow precipitate on adding a solution of KI to a solution of $SnCl_2$. The salt is sparingly soluble in cold water, but readily so in hot water. It dissolves in hydroiodic acid to form *iodostannous acid*, $HSnI_3$.

Stannous bromide and iodide are more or less similar to the chloride in their properties.

Stannous nitrate, having the composition $Sn(NO_3)_2.20H_2O$, is obtained as white, very deliquescent and unstable crystals, on cooling a solution of SnO in dil. HNO_3 (of density 1·2) to −20°C. [The action of dil. HNO_3 on metallic tin produces a mixture of stannic nitrate and stannous nitrate.] Stannous nitrate is soluble in water with extensive hydrolysis.

Stannous sulphide (SnS) can be prepared by the direct union of granules of tin and sulphur powder at elevated temperatures. It is also precipitated when H_2S gas is passed through a solution of stannous salt, acidified with dilute HCl : $SnCl_2+H_2S=SnS+2HCl$.

Stannous sulphide is a dark brown substance, insoluble in water, dilute mineral acids, as well as in solutions of alkalis and ammonium carbonate. It is, however, soluble in conc. HCl and in yellow ammonium sulphide to form stannous chloride and ammonium thiostannate respectively : $SnS+2HCl=SnCl_2+H_2S$; $SnS+(NH_4)_2S_2=(NH_4)_2SnS_3$. The solution of the thiostannate precipitates yellow stannic sulphide on acidification with dilute hydrochloric acid : $(NH_4)_2SnS_3+2HCl=SnS_2+2NH_4Cl+H_2S$.

Stannous sulphide, when heated in hydrogen, sublimes unchanged to form a lustrous crystalline product (density=5·27 ; m.p. 882°C).

Stannous sulphate can be prepared as white needles, on boiling metallic tin with copper sulphate solution, filtering off the precipitated copper and then concentrating the filtrate : $Sn+CuSO_4=Cu+SnSO_4$. It is also obtained by dissolving tin in a mixture of 1 volume conc. H_2SO_4, 2 volumes conc. HNO_3 and 3 volumes of water. The resultant solution, on concentration, yields needle-shaped crystals of stannous sulphate. The salt is readily soluble in water, but is extensively hydrolysed in solution.

Tests : In the *dry test*, tin compounds impart a brownish red colour to the microcosmic bead, when heated with a trace of copper salt in the reducing flame. Solutions of Sn(II) and Sn(IV) salts in dil. HCl precipitate the brown SnS and the yellow SnS_2 respectively, when H_2S gas is passed through them. The precipitates are soluble in yellow ammonium sulphide solution to form ammonium thiostannate. A very sensitive test of Sn(II) salts is the appearance of deep purple-red colour (*purple of Cassius*), when a few drops of gold chloride soln. is added to a weakly acidic soln. of Sn(II) salts. The reduction of $HgCl_2$ solution to Hg_2Cl_2 or metallic mercury (grey) is also often used as a test of stannous salts. A delicate test of tin salts is the *fluorescence test*. In this test, the tin compound is treated with conc. HCl and zinc dust in a small beaker. The lower part of a test tube, half-filled with water, is then dippped in the soln. of the beaker and it is then held in the Bunsen flame. A blue fluorescence is formed on the outer surface of the lower part of the test tube.

Gravimetrically, tin is estimated as SnO_2 after igniting the precipitated metastannic acid or tin cupferrate.

Volumetrically, the stannous tin can be estimated by titration with a standard iodine soln. in an inert atmosphere of CO_2.

LEAD

Symbol : Pb ; *Atomic no.* = 82 ; *Atomic wt.* = 207·2

Electronic configuration : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^2$.

Occurrence : Lead constitutes about $1{\cdot}6 \times 10^{-3}$ % of the earth's crust and as such, it is less abundant in nature than many other so-called rare elements. But, the metal is found associated in many concentrated deposits throughout the world. The metal is the stable end-product of radioactive decay of all the radio-elements, and as such, it is often found in very small amounts in the free state. The most important and widely distributed ore of lead is lead sulphide or *galena* (*PbS*) which is also usually associated with the sulphide ores of zinc, copper, iron and antimony. The ore is widely available in the U.S.A., Mexico, Canada and in Broken Hill (New South Wales). In India, galena occurs at Zawar (Rajasthan) and Hazaribag (Bihar). The other less important ores of lead are the decomposition products of galena, such as *anglesite* ($PbSO_4$) and *cerussite* ($PbCO_3$, white lead ore). Minerals of lead, like *crocoisite* ($PbCrO_4$, red lead ore), *wulfenite* ($PbMO_4$) and *stolzite* ($PbWO_4$) are available in some localities, but they have little significance as the ore of the metal.

Extraction : The metallurgical extraction of lead is principally carried out by two processes, *viz*. (i) the self-reduction process and (ii) the carbon-reduction process.

(i) **The self-reduction process :** In this method (which is also called *the Roast-reaction process*), the ore (galena) is first concentrated by the froth-floatation process to remove zinc sulphide and other gangue materials, and the dried concentrated ore is then roasted in a reverberatory furnace at 500 – 600°C in such a way that some portion of PbS is oxidised to PbO and $PbSO_4$, while the remaining portion remains unchanged :

$$2PbS+3O_2=2PbO+2SO_2\uparrow \;;\; PbS+2O_2=PbSO_4.$$

In the subsequent step, the supply of air inside the furnace is totally stopped and the roasted mass is heated to higher temperatures with the addition of small amounts of quicklime and coke. As a result, the unchanged lead sulphide reacts with PbO and $PbSO_4$ to form metallic lead and SO_2 :

$$PbS+2PbO=3Pb+SO_2\uparrow \;;\; PbS+PbSO_4=2Pb+2SO_2\uparrow.$$

The liberated metal remains in the molten state at the temperature of the furnace, and is tapped out from the bottom, while the slag collects at the surface of the molten mass and is removed. The slag consists of calcium silicate which contains considerable amount of lead. The metal is recovered from it by subsequent smelting with lime and coke in a blast furnace : $PbSiO_3+CaO=CaSiO_3+PbO$; $PbO+C=Pb+CO\uparrow$; $PbO+CO\uparrow=Pb+CO_2\uparrow$.

(ii) **The carbon-reduction process :** This is a more modern method of extracting lead and is often called the *Roast-reduction process*. Ores containing large proportions of impurities can be satisfactorily worked up by this method. In this method, the concentrated ore (obtained through froth-floatation process) is mixed with a small quantity of lime and quartz, and is oxidised by blast-roasting at high temperatures, which consists in blowing air through the above mixture. The oxidation of lead sulphide is so effected that most of it is converted to PbO. A little lead sulphate is also formed during the roasting, and it is readily transformed into lead silicate through reaction with the quartz present : $2PbS+3O_2=2PbO+2SO_2\uparrow$; $PbS+2O_2=PbSO_4$; $2PbSO_4+2SiO_2=2PbSiO_3+2SO_2\uparrow+O_2\uparrow$. The product, obtained in the above roasting process, is reduced by heating in a blast furnace with coke. $PbSiO_3$ does not, however, react directly with coke or carbon monoxide (obtained from the oxidation of coke in the furnace). But, the quicklime produced from the decomposition of limestone at the previous roasting, converts $PbSiO_3$ into PbO which is then reduced by carbon or CO : $PbSiO_3+CaO=PbO+CaSiO_3$; $PbO+C=Pb+CO\uparrow$; $PbO+CO=Pb+CO_2\uparrow$. The crude molten lead is taken out through the outlet near the bottom of the furnace.

Refining of lead : The crude metal obtained by the above processes is known as 'lead bullion'. It contains many impurities such as copper, iron, zinc, bismuth, tin, antimony, sulphur *etc.*, together with not very insignificant amounts of precious metals like silver and gold. Pure lead is soft, but the presence of the above impurities makes it hard. So, the removal of these impurities from lead or its refining is often called the '*softening of lead*'.

The refining or softening of crude lead is carried out in two operations. At first, the lead bullion is melted on the shallow hearth of a reverberatory furnace and the melt is agitated regularly with an access of air, when the impurities (except Bi, Ag and Au) are converted into their oxides and rise as a scum on the surface of the liquid ; arsenic and sulphur are volatilised as As_2O_3 and SO_2. A small portion of lead is also converted into lead monoxide or lead arsenate and antimonate which also collect at the surface along with the scum. The scum is skimmed off. The metal, so obtained, is sometimes re-melted on an inclined hearth of a furnace (*liquation*), so that the molten lead slowly runs down, leaving behind the relatively infusible impurities. The product is then subjected to *de-silverisation* by Parke's or Pattinson's process to recover gold and silver. [For details of these operations, see 'the extraction of silver' at page 420, vol. I of this book.]

Crude lead is now-a-days softened by an electrolytic method, known as the **Betts process.** In this method, a solution of lead silicofluoride, acidified with hydrofluosilicic acid, is electrolysed with de-silverised lead blocks as anodes and thin strips of pure lead as cathode. [A little gelatine is added to the electrolyte to make the deposit of lead in the cathode in the compact form.] On carrying out the electrolysis, lead is deposited on the cathode and the impurities like Cu, Bi, Sb, Au and Ag are precipitated as the anode sludge.

Properties : Lead is a bluish white metal (density=11·34 ; m. p.=327·4°C ; b. p.=1750°C). It has a bright lustre at the freshly cut surface, but it readily tarnishes in air. It is very soft and can be cut with a knife. It is highly malleable and ductile, so that the metal can be rolled into thin sheets and drawn into fine wires. Lead marks paper.

Lead is unaffected by dry air ; but moist air attacks the metal and forms basic lead carbonate which protects it from further action. When melted in air, the molten lead becomes covered with a layer of grey oxide (commonly known as *lead dross*), which is first converted to the yellow monoxide (*litharge*) and ultimately to red lead or *minium* (Pb_3O_4) at higher temperatures : $2Pb+O_2=2PbO$; $6PbO+O_2=2Pb_3O_4$. Water, free from dissolved air (or oxygen), does not attack lead ; but when dissolved air (or oxygen) is present in water, lead hydroxide is formed. As lead hydroxide is somewhat soluble in water and is poisonous, drinking water, flowing through lead pipes, causes serious lead-poisoning. [Hard water, containing soluble carbonates and/or sulphates, does not react with lead because of the formation of protective coating of insoluble lead carbonate and/or lead sulphate. Soft water, treated previously with chalk or lime, does not also attack lead pipes.] Although lead is placed immediately above hydrogen in the electrochemical series, the metal is not usually attacked by dilute acids due to the facts that (i) the evolution of hydrogen on pure lead takes place at a considerable *overvoltage* and (ii) in many cases, insoluble coating of the lead salt of the reacting acid stops further reaction between the acid and the metal. Thus, lead is practically unaffected in absence of air by dil. and conc. HCl, H_2SO_4 and HF in the cold. [But, in presence of atmospheric oxygen, lead is attacked by all acids, including the very weak acids like acetic acid.] Conc. HCl slowly dissolves lead on boiling (complex-formation probably augments this dissolution) : $Pb+2HCl=PbCl_2+H_2\uparrow$; $PbCl_2+2HCl=H_2[PbCl_4]$. Conc. H_2SO_4 attacks lead above 200°C. with the evolution of sulphur dioxide : $Pb+2H_2SO_4=PbSO_4+SO_2\uparrow+2H_2O$. Dilute nitric acid readily dissolves lead at all temperatures :

$3Pb+8HNO_3=3Pb(NO_3)_2+2H_2O+2NO$. Hot and conc. HNO_3 attacks lead, but the initial reaction is soon stopped due to the fact that the produced lead nitrate, being insoluble in conc. HNO_3, serves as a protective coating on the surface of the metal: $Pb+4HNO_3=Pb(NO_3)_2+2H_2O+2NO_2$. Strong alkali solutions slowly react with lead to form alkali plumbite and hydrogen: $Pb+2NaOH=Na_2PbO_2+H_2\uparrow$. Lead combines directly, when heated, with sulphur, selenium, tellurium and halogens to form the corresponding binary compounds. It also readily alloys with other metals and forms amalgam with mercury. The metal is precipitated from soluitons of its salts as beautiful interlaced crystals (*Lead tree*) by the more electropositive metals like zinc, tin or iron. Metallic lead has a tendency to *flow out* at ordinary temperatures, and it is increased on heating.

Alloys of lead: Lead forms many useful alloys, the metal being usually hardened by such alloying. Some important alloys of lead are: (*i*) *Type metal* (Pb, 80%, Sb, 15%; Sn, 5%), (*ii*) *Solder* (Pb, 50%; Sn, 50%), (*iii*) *Pewter* (Pb, 20%; Sn, 80%). Brass and bronze also contain lead.

Uses: Lead is used for making pipes, for covering electrical cables, roofs, chambers in H_2SO_4 plants (lead chamber process), for fabricating crucibles, evaporating pans, plates for accumulators, cores of bullets and for making shots. Alloys of lead have many important uses, *e.g.* in making types, solders, accumulator plates, bearings *etc.* Many lead compounds (white lead, Pb_3O_4, $PbCrO_4$ *etc.*) are used as pigments.

Compounds of lead.

Lead forms two series of compounds—the *plumbous* and the *plumbic* compounds—in which the metal exhibits bivalency and tetravalency respectively. The lead (II) salts are more stable than the lead (IV) salts which possess a strong tendency to pass into the Pb(II) state, and as such, the Pb(IV) compounds are strong oxidising agents: $Pb^{+4}+2e \longrightarrow Pb^{+2}$. In the formation of the Pb(II) compounds, two electrons in the valence-shell of the metal remain as the *inert pair* and the other two electrons are used in bonding, while in the Pb(IV) salts, all these four electrons are involved in the formation of mainly covalent bonds. Free Pb^{+4} ions cannot exist in any appreciable concentrations in aqueous solution because of the hydrolysis into PbO_2: $Pb^{+4}+2H_2O=PbO_2+4H^+$.

Lead (II) Compounds.

Lead monoxide (PbO) can be obtained in two different forms, *viz.* the yellow coloured *massicot* and the yellowish red *litharge*. Of the two forms, litharge is the stable modification at ordinary temperatures (and hence is chemically less active), less soluble and more dense than massicot. It is prepared on a large scale through the oxidation of molten lead by a blast of air. [It is formed during the cupellation of argentiferous lead : See Vol. I. p.422.] Massicot is obtained as a yellow powder by the thermal decomposition of lead nitrate or lead carbonate : $PbCO_3=PbO+CO_2$; $2Pb(NO_3)_2=2PbO+4NO_2+O_2$. Massicot is transformed into litharge on prolonged boiling with water. All other oxides of lead produce litharge on heating above 550°C.

Lead monoxide is insoluble in water, but dissolves readily in acids to form lead (II) salts. It is slightly soluble in dilute alkali solutions, but slowly dissolves in hot, concentrated alkalis to form plumbites. It is thus dominantly a basic oxide with some amphoteric character : $PbO+2HNO_3=Pb(NO_3)_2+H_2O$; $PbO+2NaOH=Na_2PbO_2+H_2O$. On heating in air for some time at about 450°C, it is oxidised to red lead (massicot is generally used to manufacture red lead). When heated in a current of hydrogen or carbon monoxide, or when a mixture of PbO with coke or potassium cyanide is heated, reduction to metallic lead takes place : $PbO+H_2=Pb+H_2O$; $PbO+C=Pb+CO$.

Lead monoxide is used as paints and also in the preparation of varnishes, plasters, enamels, glazes, flint glass, red lead and other lead salts, as well as in the vulcanisation of rubber.

Lead sesquioxide (Pb_2O_3) results as a reddish yellow powder by the action of oxidising agents like hypochlorite, bromine or hydrogen peroxide on a cold solution of PbO in caustic potash : $2PbO+NaOCl=Pb_2O_3+NaCl$. The oxide is insoluble in water, but dissolves in acids to form lead (II) salts and PbO_2 : $Pb_2O_3+3HNO_3=Pb(NO_3)_2+PbO_2+H_2O$. The chemical reaction suggests that lead sesquioxide is a mixture of PbO and PbO_2 in 1 : 1 molecular proportions ; but, it may also be regarded as lead (II) metaplumbate, $Pb^{II}(Pb^{IV}O_3)$.

Lead hydroxide [$Pb(OH)_2$] is obtained as a white gelatinous precipitate, when alkali solutions (avoiding excess) are added to the solutions of lead (II) salts : $Pb^{++}+2OH^-=Pb(OH)_2$. It is slightly soluble in water, the aqueous solution being alkaline. It is, however, amphoteric in nature, and dissolves in acids to form lead (II) salts and in alkalis to form plumbites (but, the plumbites are readily hydrolysed in aqueous solution to re-form lead hydroxide) : $Pb(OH)_2 + 2HNO_3 = Pb(NO_3)_2 + 2H_2O$; $Pb(OH)_2 + 2NaOH \rightleftharpoons Na_2PbO_2 + 2H_2O$. If the hydroxide is dehydrated at 100°C or above, litharge is formed ; but, on dehydration at lower temperatures, massicot is obtained.

Lead (II) halides.

Lead (II) fluoride (PbF_2) is prepared as a white powder (m.p.=818°C) by adding a solution of a fluoride to lead nitrate solution, or by the action of hydrofluoric acid on lead hydroxide or carbonate. It is sparingly soluble in water, but it dissolves easily in hydrochloric and nitric acids.

Lead (II) chloride ($PbCl_2$) is prepared by the action of hydrochloric acid on lead monoxide or basic lead carbonate, or by dissolving metallic lead in dilute HNO_3 and precipitating the salt by adding hydrochloric acid : $PbO + 2HCl = PbCl_2 + H_2O$; $Pb_3(OH)_2(CO_3)_2 + 6HCl = 3PbCl_2 + 2CO_2 + 4H_2O$; $3Pb + 8HNO_3 = 3Pb(NO_3)_2 + 2NO + 4H_2O$; $Pb(NO_3)_2 + 2HCl = PbCl_2 + 2HNO_3$.

Lead chloride forms white lustrous (silky) crystals (m.p.=498°C), sparingly soluble in cold water, but comparatively more soluble in hot water. It also dissolves in conc. hydrochloric acid to form $H_2[PbCl_4]$, which decomposes on dilution, with the precipitation of lead (II) chloride : $PbCl_2 + 2HCl \rightleftharpoons H_2[PbCl_4]$. The dry salt can be distilled without decomposition in a current of carbon dioxide ; but, it is hydrolysed to the oxychloride when heated in air (the moisture of air brings about the hydrolysis at the elevated temperature). Complex compounds of lead chloride with pyridine and thiourea are known.

Lead bromide ($PbBr_2$) is obtained as white, lustrous, needle-shaped crystals by methods similar to those of $PbCl_2$. The compound melts at 373°C into a red liquid. It slowly darkens on exposure to light, due to decomposition into metallic lead. Its solubility in water is more or less similar to that of $PbCl_2$.

Lead iodide (PbI_2) is formed as a yellow precipitate when a soluble iodide is added to a solution of lead (II) salts. On recrystallisation from hot water, lead (II) iodide forms beautiful golden yellow sparkling leaflets (golden spangles), melting at 412°C. On heating, it first turns brick-red and then brown ; but, the original color is regained on cooling. Lead (II) iodide is much less soluble in water that $PbCl_2$ and the aqueous solution is quite colourless. This is due to the fact that, in aqueous solution, the salt is present almost completely in the dissociated state, *i.e.* as Pb^{++} and I^- ions, both of which are colourless. Lead iodide dissolves in KI solution to form colourless complex salt, $K_2[PbI_4]$, which is decomposed on dilution, with the precipitation of lead (II) iodide : $PbI_2+2KI \rightleftharpoons K_2[PbI_4]$.

Lead (II) sulphide (PbS) occurs in nature as *galena*, the principal ore of the metal. The sulphide is thrown down as a black precipitate when hydrogen sulphide is passed through a solution of lead (II) salts : $Pb^{++}+S^{2-}=PbS\downarrow$. In presence of excess HCl in solution, a yellow or red precipitate of $PbCl_2.PbS$ is often formed, but it is transformed into black PbS on dilution with water and passing an excess of hydrogen sulphide : $2PbCl_2+H_2S=PbCl_2.PbS+2HCl$. Lead sulphide may also obtained as a grey mass by heating the metal in sulphur vapour.

When heated in air, lead sulphide is oxidised to lead sulphate and lead dioxide : $2PbS+3O_2=PbSO_4+PbO_2$. It is insoluble in water, dil. HCl and dil. H_2SO_4, but it dissolves readily in hot, dil. HNO_3, with the liberation of sulphur : $3PbS+8HNO_3=3Pb(NO_3)_2+2NO+4H_2O+3S\downarrow$. [Conc. HNO_3, however, oxidises it into lead sulphate.] It also dissolves on boiling with conc. HCl to form lead (II) chloride and hydrogen sulphide : $PbS+2HCl=PbCl_2+H_2S\uparrow$. Hydrogen peroxide and ozone oxidise lead sulphide into lead (II) sulphate : $PbS+4H_2O_2=PbSO_4+4H_2O$; $PbS+4O_3=PbSO_4+4O_2$.

Lead (II) sulphate ($PbSO_4$) occurs native as *anglesite*. It is obtained as a heavy white precipitate when a soluble sulphate or dil. H_2SO_4 solution is added to a solution of lead (II) salts : $Pb^{++}+SO_4^{2-}=PbSO_4\downarrow$. The compound is sparingly soluble in water, but dissolves to a considerable extent in conc. acids. It is also soluble in hot solutions of sodium acetate or ammonium acetate, and it is due partly to complex formation and partly because of the formation of feebly dissociated lead acetate. [This property of $PbSO_4$ is taken advantage of in differentiating $PbSO_4$ from $BaSO_4$.]

Lead (II) chromate ($PbCrO_4$) occurs naturally as *crocoisite*. As an important pigment, it is prepared on a large scale by mixing a solution of lead acetate with a solution of potassium chromate, acidified with dil. H_2SO_4 at ordinary temperature : $Pb^{++}+CrO_4^{2-}=PbCrO_4\downarrow$. [Use of neutral chromate solution precipitates $PbCrO_4$ of darker shades.] Potassium dichromate solution precipitates $PbCrO_4$ incompletely from a neutral solution of lead (II) salt :

$$Pb^{++}+Cr_2O_7^{2-}+H_2O=PbCrO_4+H_2CrO_4.$$

Lead chromate is a yellow compound, extremely insoluble in water and acetic acid, but dissolves in strong mineral acids and alkali solutions, forming soluble lead (II) salts and plumbites respectively: $PbCrO_4+4NaOH=Na_2PbO_2+Na_2CrO_4+2H_2O$. Lead chromate is a pigment (*chrome yellow*). When digested with dil. alkali solutions, lead chromate forms the basic salt, $PbCrO_4. PbO$, as a red mass which is used as a pigment (*chrome red*). A mixture of chrome red and chrome yellow is also used as a pigment (*chrome orange*).

Lead nitrate [$Pb(NO_3)_2$] is prepared by dissolving litharge, basic lead carbonate or the metal itself in hot, dilute nitric acid and crystallising the product from acidic solution. It is also obtained as a by-product during the preparation of lead dioxide from red lead.

Lead nitrate forms colourless crystals, highly soluble in water without any hydrolysis. It is decomposed on heating to give lead monoxide, nitrogen dioxide and oxygen: $2Pb(NO_3)_2=2PbO+4NO_2+O_2$. It is an oxidising agent and is used in match industry and also for the preparation of other lead (II) compounds.

Lead (II) carbonate ($PbCO_3$) occurs in nature as *cerussite*. It may be artificially prepared by adding a solution of lead (II) acetate or lead (II) nitrate to a solution of sodium bicarbonate or ammonimum carbonate. [The use of Na_2CO_3 solution produces the basic salt, $Pb(OH)_2. 2PbCO_3$ (*white lead*)]. Lead carbonate is also precipitated on passing a stream of CO_2 into a cold, dilute solution of lead (II) acetate.

Lead carbonate is practically insoluble in water, but it dissolves in acids and ammonium acetate solution. When heated above 300°C, it decomposes into lead monoxide and carbon dioxide:

$$PbCO_3=PbO+CO_2.$$

White lead or Basic lead carbonate [$2PbCO_3.Pb(OH)_2$] is an important white pigment and is always prepared on a large scale by various processes, of which the oldest *Dutch process* is largely used.

(i) **The Dutch process:** In this process, white lead is obtained by the prolonged simultaneous action of air, moisture, acetic acid vapours and carbon dioxide on sheets of metallic lead. The actual operation consists in spreading a layer of dung or spent tan-bark on the floor of brick-built chamber and a number of glazed earthen pots, containing some dilute acetic acid, are embedded in the layer. The earthen pots are fitted with perforated shelfs at the middle, and thin lead sheets, rolled in the form of spirals, are placed on them. The pots are loosely covered with a light board, over which similar layer of dung and earthen pots are arranged, till the chámber is full with the successive rows. The chamber is then covered with a shed and left as such for several weeks (5-8 weeks). During this period, the fermentation of dung or tan-bark produces CO_2 and provides necessary warmth required for the slow evaporation of acetic acid and water. Acetic acid vapours react with lead in presence of air and moisture to form basic lead acetate which is ultimately converted to basic lead carbonate by CO_2. The liberated acetic acid and lead acetate enter again into the reactions and the process continues, until the evolution of CO_2 ceases or all the metal is used up.

$$2Pb+4CH_3COOH+O_2=2Pb(CH_3COO)_2+2H_2O\ ;$$
$$Pb(CH_3COO)_2+H_2O=Pb(OH)(CH_3COO)+CH_3COOH\ ;$$
$$6Pb(OH)(CH_3COO)+2CO_2=2PbCO_3.Pb(OH)_2+3Pb(CH_3COO)_2 +2H_2O.$$

After the completion of the reactions, the lead sheets inside the earthen pots become thickly covered with white lead. These are scraped off, ground finely to separate any unchanged lead, washed with water and dried.

(ii) In the **German process**, white lead is manufactured by essentially the similar reactions. Lead sheets are suspended in chambers, into which CO_2 and acetic acid vapours are simultaneously passed.

(iii) In the **French process**, which operates in the *wet way*, white lead is manufactured by passing CO_2 into a solution of basic lead acetate (obtained by dissolving PbO in boiling lead acetate solution).

(iv) In the **electrochemical process**, a solution containing NaCl and Na_2CO_3 is electrolysed with lead sheet anodes, and CO_2 is passed through the electrolyte during the electrolysis. Lead, dissolving out from the anodes, is immediately precipitated as basic lead carbonate during the process :

$$Pb=Pb^{++}+2e^-;\ 3Pb^{++}+2OH^-+2CO_3^{2-}=2PbCO_3.Pb(OH)_2.$$

White lead is a heavy, compact, amorphous powder which mixes intimately with oil. It has the greatest covering power of all the white pigments ; but, it suffers from the drawbacks that it is poisonous and it becomes dark gradually in air containing small amounts of hydrogen sulphide (due to the formation of PbS).

Lead (II) acetate [$Pb(CH_3COO)_2$] is obtained as colourless crystals of the trihydrate, $Pb(CH_3COO)_2.3H_2O$, when a solution of lead monoxide in hot, dilute acetic acid is crystallised. It is generally known as the *sugar of lead*, because of its intensely sweet taste ; but, the compound is highly poisonous. The compound is highly soluble in water. The hydrated salt melts at 75°C, but the anhydrous salt has a melting point of 280°C. It forms basic lead acetate, when boiled with lead monoxide.

Lead acetate is used in medicine and also as an important laboratory reagent. It is also employed for the production of pigments like *chrome yellow* and *chrome red*.

Lead (IV) Compounds.

Lead hydride or Plumbane (PbH_4) is a highly unstable gas (b.p.=−13°C), and was obtained (Paneth, 1920) through electrolytic reduction of a lead cathode at high current density. The hydride is readily decomposed at ordinary temperatures and forms a metallic mirror of lead when it is passed through a hot tube. [The formation of the hydride was actually known by this mirror-test.] The hydride has also been reported (Schulze, 1929) to be formed by the action on atomic hydrogen on lead.

Lead dioxide (PbO_2) is obtained by the oxidation of lead (II) salts either electrolytically (by platinum electrodes) or chemically (by chlorine, bromine, hypochlorite *etc.*). It can also be prepared by dissolving out lead (II) oxide from red lead (Pb_3O_4) by dilute HNO_3, or by the oxidation of lead acetate by bleaching powder :

$$Pb_3O_4+4HNO_3=PbO_2+2Pb(NO_3)_2+2H_2O\ ;$$

$$Pb(CH_3COO)_2+Ca(OCl)Cl+H_2O=PbO_2+2CH_3COOH+CaCl_2.$$

[In the electrolytic process, a solution of NaCl, containing suspended lead monoxide (PbO), is electrolysed with Pt-electrodes. PbO is oxidised to PbO_2 by the hypochlorite formed electrolytically and the product is deposited at the anode.]

Lead dioxide is a chocolate-brown powder, practically insoluble in water and dilute acids. But, on heating with conc. HCl or conc. H_2SO_4, it reacts with the evolution of chlorine or oxygen respectively : $PbO_2+4HCl=PbCl_2+2H_2O+Cl_2$; $2PbO_2+2H_2SO_4=2PbSO_4+2H_2O+O_2$. Its acidic character is more pronounced and it reacts, when heated, with strongly basic oxides or hydroxides to form plumbates : $PbO_2+Na_2O=Na_2PbO_3$; $PbO_2+2NaOH=Na_2PbO_3+H_2O$.

Lead dioxide is a strong oxidant. When a stream of SO_2 at ordinary temperature is passed over lead dioxide, it becomes white-hot, and lead sulphate is formed : $PbO_2+SO_2=PbSO_4$. When it is rubbed with easily combustible substances like sulphur or red phosphorus, inflammation takes place with the formation of lead sulphide or lead phosphide respectively. A manganous salt is oxidised to pink permanganic acid ($HMnO_4$), on heating with conc.

HNO_3 and lead dioxide : $2MnSO_4+5PbO_2+6HNO_3=2HMnO_4+2PbSO_4+3Pb(NO_3)_2+2H_2O$. In alkaline medium, chromic hydroxide is oxidised to chromate (yellow colour) by lead dioxide : $3Cr(OH)_3+10KOH+3PbO_2=2K_2CrO_4+3K_2PbO_2+8H_2O$. Oxalic acid is oxidised to CO_2 when heated with PbO_2 in presence of nitric acid : $(COOH)_2+PbO_2+2HNO_3=2CO_2+Pb(NO_3)_2+2H_2O$. Lead dioxide is stable upto 300°C. When heated above 300°C (but below 450°C), it loses oxygen to form lead monoxide ; at 450 – 500°C, red lead is formed : $2PbO_2=2PbO+O_2$; $6PbO_2=2Pb_3O_4+2O_2$.

[PbO_2 is *not* a peroxide, as it does not produce H_2O_2 on treatment with acids. Its structure is that of a tetravalent lead compound (O=Pb=O), which does not contain the so-called *peroxo-bridge*.]

Lead dioxide is used in the anode of lead accumulators, in the preparation of matches and as an oxidising agent in the laboratory.

Red lead or Minium (Pb_3O_4) is prepared by heating lead monoxide (litharge or massicot, PbO) in air at 450 – 500°C for a few hours : $6PbO+O_2=2Pb_3O_4$. It forms a brilliant red powder which is practically insoluble in water. It dissociates into PbO and O_2 on heating above 550°C. The red compound darkens on heating, but the original colour is restored on cooling. Red lead dissolves in nitric acid to form lead dioxide and lead (II) nitrate : $Pb_3O_4+4HNO_3=PbO_2+2Pb(NO_3)_2+2H_2O$. The reactions and the crystal structure of Pb_3O_4 indicate that it is not merely a mixture of PbO and PbO_2, but it should be considered as lead (II) orthoplumbate, $Pb^{II}_2(Pb^{IV}O_4)$. Like the dioxide, red lead reacts with hot and concentrated H_2SO_4 and HCl with the evolution of O_2 and Cl_2 respectively : $2Pb_3O_4+6H_2SO_4=6PbSO_4+6H_2O+O_2$; $Pb_3O_4+8HCl=3PbCl_2+4H_2O+Cl_2$.

Red lead is extensively used as an oil paint (mixed with linseed oil) for the protection of iron against rusting and also for luting joints of iron pipes in plumbing work. It is also used sometimes as an oxidant.

Lead tetrahalides.

Lead tetrafluoride (PbF_4) is obtained as a white crystalline substance on passing fluorine gas over plumbous fluoride (PbF_2), heated above 250°C. The compound is not very stable, but the stable complex fluoplumbates like $Na_2[PbF_6]$, $Rb_2[PbF_6]$, $Cs_2[PbF_6]$, $K_3H[PbF_8]$, $(NH_4)_3H[PbF_8]$ *etc.* are known.

Lead tetrachloride ($PbCl_4$) is prepared by first dissolving PbO_2 in ice-cold conc. HCl (saturated with chlorine), and adding ammonium chloride to the resultant yellow solution. A yellow precipitate of ammonium chloroplumbate is thus formed. The precipitate is then dissolved in cold conc. H_2SO_4, when lead tetrachloride is formed as a heavy, yellow oil which can be easily separated from the reaction-mixture : $PbO_2+6HCl=H_2PbCl_6+2H_2O$; $H_2PbCl_6+2NH_4Cl=(NH_4)_2PbCl_6\downarrow+2HCl$; $(NH_4)_2PbCl_6+H_2SO_4=PbCl_4+(NH_4)_2SO_4+2HCl$.

Lead tetrachloride is a heavy (sp. gr.=3·18 at 0°C), yellow, fuming oily liquid, freezing at −15°C to yellow crystals. The compound is not very stable. It is easily decomposed on warming to evolve chlorine and it explodes on heating at 105°C : $PbCl_4=PbCl_2+Cl_2$. It is hydrolysed by water to form lead dioxide and hydrochloric acid : $PbCl_4+2H_2O=PbO_2+4HCl$.

Lead tetrabromide (**$PbBr_4$**) and lead tetra-iodide (PbI_4) are not known, probably because of the strong oxidising power of Pb (IV) and the reducing power of Br^- and I^-, which results in the Pb (II) compounds being always formed. Complex hexabromo- and hexa-iodoplumbates of the alkali metals are, however, known.

Lead (IV) sulphate, [$Pb(SO_4)_2$], is obtained as yellow granular deposits on the anode, when 80% H_2SO_4 solution is electrolysed between lead electrodes below 30°C using a porous diaphragm. The compound is hydrolysed by water into lead dioxide : $Pb(SO_4)_2+2H_2O=PbO_2+2H_2SO_4$.

Lead tetra-acetate, $Pb(CH_3COO)_4$, is prepared by dissolving red lead in warm glacial acetic acid, passing chlorine gas into the solution and then cooling. Lead (II) chloride is precipitated and filtered off. [The treatment with chlorine gas oxidises some of the lead (II) acetate which is simultaneously formed.] The compound is obtained, through concentration of the solution, as white needles (m. p. 175°C). It is readily hydrolysed by water to give lead dioxide. It is soluble in organic solvents. $Pb_3O_4+8CH_3COOH=Pb(CH_3COO)_4+2Pb(CH_3COO)_2+4H_2O$; $2Pb(CH_3COO)_2+Cl_2=Pb(CH_3COO)_4+PbCl_2$.

Lead tetra-acetate is used as an oxidising agent in organic chemistry.

Lead tetraethyl, [$Pb(C_2H_5)_4$], is obtained as a colourless liquid (density=1·65) by the reaction of zinc alkyl or Grignard reagent (RMgBr) with lead (II) chloride.

Lead (II) diethyl, [$Pb(C_2H_5)_2$], which is first formed, disproportionates into lead (IV) tetraethyl and metallic lead : $PbCl_2+Zn(C_2H_5)_2=Pb(C_2H_5)_4+ZnCl_2$; $2Pb(C_2H_5)_2 =Pb+Pb(C_2H_5)_4$. The liquid is not hydrolysed by water, and it can be distilled undecomposed under reduced pressure. It is used as an anti-knock agent in the fuels of internal combustion engines.

Lead Accumulator or Lead storage cell.

In principle, a lead accumulator consists of two perforated lead plates dipped into dilute H_2SO_4 of specific gravity 1·15–1·20, contained in a rectangular glass vessel. One of the lead plates is packed with PbO_2 (positive plate) and the other with spongy metallic lead (negative plate). In actual practice, several such plates are alternately arranged in an accumulator, and the plates of each kind are connected together to form the two poles of the battery. If the two poles are joined by an external conductor, a current of electricity flows from PbO_2-plate (brown coloured) to the lead plate (grey coloured).

A lead accumulator is used to store up electrical energy which may be utilised when needed. The electrical energy obtained from the apparatus is generated at the expense of the energy of the chemical reaction taking place within the cell, when the two poles are connected by an external conductor. When electric current is drawn from an accumulator, it becomes 'discharged', and in this process, the PbO_2 in the positive plate gives up positive electricity (or takes up electron) to pass into divalent lead ion : $PbO_2+4H^++2e \rightarrow Pb^{++}+2H_2O$. At the negative plate, metallic lead is simultaneously oxidised as Pb^{++} ion and goes into solution : $Pb \rightarrow Pb^{++}+2e$. The Pb^{++} ions formed in both the reactions combine with the sulphuric acid in the cell to form insoluble $PbSO_4$ which is deposited on the two plates. Thus, the reactions at the two electrodes are :

$$PbO_2+4H^++SO_4^{2-}+2e=PbSO_4+2H_2O\ ;$$

$$Pb+SO_4^{2-}=PbSO_4+2e.$$

Combining the above two reactions, we get the total chemical reaction in the above discharge process as,

$$PbO_2+Pb+2H_2SO_4=2PbSO_4+2H_2O.$$

The e. m. f. of a fully charged accumulator is 2 volts. On drawing current from it, the e. m. f. gradually falls and reaches a lower limit of 1.8 volts, when the flow of current practically stops. The accumulator is then to be *'charged'* to raise the e. m. f. to the required value. This is done by applying an external potential, larger than 2 volts, in the reverse direction,—*i.e.* the positive pole of the external source is joined to the positive pole of the accumulator. As a result, chemical reactions, reverse of those of the discharge process, occur at the two electrodes. In the positive plate, Pb^{++} ions are oxidised to Pb^{+4} ions, which immediately react with water to deposit PbO_2 on the plate : $Pb^{++} - 2e \rightarrow Pb^{+4}$; $Pb^{+4} + 2H_2O \rightarrow PbO_2 + 4H^+$. In the negative plate, lead is deposited by the discharge (or the reduction) of Pb^{++} : $Pb^{++} + 2e \rightarrow Pb$.

During discharge, water is formed and the concentration of H_2SO_4 in the accumulator falls, while during charging, the concentration of the acid increases again due to the consumption of water. Thus, by measuring the concentration (or the sp. gravity) of the acid, the state of charge of an accumulator can be judged. If the charging process of a discharged accumulator is continued even after all the $PbSO_4$ that was formed is depleted, hydrogen is evolved at the negative electrode and oxygen at the positive electrode of the cell.

Tests : (i) Lead compounds, reduced in a charcoal-block with anhydrous Na_2CO_3, forms a malleable bead of lead, surrounded by yellow incrustation of PbO. The bead marks paper and dissolves in dil HNO_3, and the resultant soln. responds to the characteristic tests of Pb^{++} (given below). (ii) A soln. of lead salt gives a white ppt. on treatment with dil. HCl. The ppt. dissolves in boiling water, but reappears as shining crystals on cooling. (iii) A soln. of lead salt gives a yellow ppt. on treatment with KI soln. The ppt. dissolves in boiling water, but reappears as shining golden spangles on cooling the soln. (iv) A soln. of lead salt gives a yellow ppt. with a soln. of potassium chromate. The ppt. is insoluble in acetic acid.

Gravimetrically, lead is estimated as lead sulphate or lead chromate after drying at 120°C. Alternatively, the precipitated $PbCrO_4$ may be dissolved in dil. HCl, potassium iodide added and the liberated iodine estimated by standard thiosulphate soln.

[1 ml. N/10 $Na_2S_2O_3$ soln. $\equiv$ 0·0069 gm. of lead.]

CHAPTER XVI

GROUP VB ELEMENTS : THE NITROGEN FAMILY

The group VB of the Periodic Table consists of five elements, *viz.* nitrogen, phosphorus, arsenic, antimony and bismuth, and it is also called the nitrogen family. Of these five elements, only phosphorus occurs abundantly in nature (0.118% of the earth's crust), occupying the tenth position in the order of natural abundance. Though nitrogen occupies almost 78% (by volume) of our atmospheric air, its relative abundance is only 5×10^{-3} % and hence, is not as abundant as one generally thinks. The relative abundances of As, Sb and Bi are 4.5×10^{-3} %, 5×10^{-4} % and 1.8×10^{-5} % respectively in the earth's crust.

All the members of this group are '*p*'-block elements with ns^2np^3 configuration in their *outermost* or *valence-shell.* The regular variation of the important physical and chemical characteristics with *atomic number* (as predicted by the Periodic Law and reflected in the Periodic Classification of elements) is clearly illustrated in this group. In this group, there is a gradual change from a true non-metal (nitrogen) to a true metal (bismuth), through the *metalloid*, arsenic.

The electronic configurations of the Gr. VB elements, along with some of their most important properties, are summarised in the following table (page 98, table 16·1) :

Variation in physical states of occurrence and the allotropic modifications : The elements of this group exhibit a gradual transition in their physical states of occurrence. The first member, nitrogen, is a gas and can be liquified at a very low temperature (−195.8°C). The second element, phosphorus, is a soft and low-melting solid (m. p. 44.1°C) which passes into the vapour state at 280°C. The elements following phosphorus, *viz.* As, Sb and Bi are all solids. The boiling points of the elements of this group increase with the increase in atomic number. The melting points increase from nitrogen to arsenic and then decrease, with bismuth having an unusually low melting point.

TABLE 16·1

PROPERTIES	ELEMENTS				
	Nitrogen	Phosphorus	Arsenic	Antimony	Bismuth
Atomic number	7	15	33	51	83
Electronic configuration	$\boxed{\text{He}}\ 2s^2 2p^3$	$\boxed{\text{Ne}}\ 3s^2 3p^3$	$\boxed{\text{Ar}}\ 3d^{10} 4s^2 4p^3$	$\boxed{\text{Kr}}\ 4d^{10} 5s^2 5p^3$	$\boxed{\text{Xe}}\ 4f^{14} 5d^{10} 6s^2 6p^3$
Atomic weight	14.008	30.98	74.91	121.76	209.00
Atomic volume of solid (c.c.)	15.95	16.9 (white phosphorus)	13.13	18.50	21.32
Atomic radius (Å)	0.74	1.10	1.21	1.41	1.52
Density (of solid) gm/c.c.	0.8792 (at −180°C)	1.8232 (white phosphorus)	5.7	6.58	9.8
Ionization potential (ev.) 1st. 2nd. 3rd.	 14.5 29.6 47.4	 11.0 19.7 30.2	 10.0 20.1 28.0	 8.6 18.0 24.7	 8.0 16.6 25.4
Electronegativity (Pauling's scale)	3.0	2.1	2.0	1.9	1.9
Oxidation states	−3, +1, +2, +3, +4, +5	−3, +1, +3, +4, +5	−3, +3, +5	−3, +3, +5	+3, +5
M. P. (°C)	−210	44.1	814.5 *at* 36 *atm*	630.5	271
B. P. (°C)	−195.8	280.5	610 (Subl.)	1380	1450

Existence of allotropic modifications is a special feature of this group. Except bismuth, all the other elements exhibit allotropy. In the solid state, nitrogen exists in two forms, (i) **α-nitrogen** with cubic lattice and (ii) **β-nitrogen**, with a hexagonal lattice. Phosphorus exists in three allotropic forms, **white phosphorus, red phosphorus** and **black phosphorus.** The three allotropic modifications of arsenic are the **grey, yellow** and **black arsenic.** Antimony also exists in three allotropic modifications, *viz.* **metallic antimony, α-antimony** and the **explosive antimony.**

Atomic volume and atomic radius : Following the general principles of the periodic classification of elements, the atomic volumes and the atomic radii of the elements of this group increase with the increase in atomic number. The only exception is arsenic, which has an unusually low atomic volume (see table 16·1).

Ionization potential : The ionization potentials of the members of Gr. VB decrease down the group, as the atomic number and and atomic volume increase.

Metallic and non-metallic character : Since the metallic character of an element is associated with comparatively large atomic volume and low ionization potential, the metallic character increases down the group with the increase in atomic number. Thus, nitrogen and phosphorus are pronounced non-metals, while antimony and bismuth are metals, with arsenic representing the intermediate **metalloid** character. Bismuth is a true metal and antimony, though predominantly metallic, possesses some metalloid character. The gradual transition from non-metallic to metallic character is manifested in the following properties.

(*a*) *Change in conductivity* : Conductivity gradually increases from the non-conductors nitrogen and phosphorus, (which are pronounced non-metals) to antimony and bismuth (which conduct electricity and heat), while arsenic is a poor conductor.

(*b*) *Basicity of the hydrides* : The basic character of the hydrides decreases sharply from NH_3 to BiH_3, which is indicative of the increase in metallic character with the increase in atomic number.

(*c*) *Nature of the oxides* : Acidity of the oxides (like the trioxides of the general formulae R_2O_3) decreases from nitrogen to bismuth. Thus, N_2O_3, P_4O_6 and As_4O_6 are acidic and dissolve in water forming the '*ous*' acids, of which As_4O_6 is least acidic. Sb_4O_6 is amphoteric and is insoluble in water, while Bi_2O_3 is a distinctly basic oxide.

(*d*) *Strength of the oxyacids*: Strength of the oxyacids of these elements (the '*ic*' acids) decreases rapidly from nitrogen to bismuth, indicating the increase in metallic character. HNO_3 is the strongest acid, and the strength sharply decreases in H_3PO_4 and H_3AsO_4, while H_3SbO_4 is amphoteric and H_3BiO_3 [rather $Bi(OH)_3$] is distinctly basic.

Electron affinity and electronegativity : Both these properties decrease down the group with the increase in atomic number, as is reflected in the gradual increase of the metallic character from nitrogen to bismuth.

Decrease in ionization potential and electron-affinity of these elements with the increase of atomic number implies that the heavier members would occur in positive oxidation states in combination with the more electronegative elements of Gr. VIB and VIIB.

Nature of bonding : The valence-shell electronic configuration of the Gr. VB elements is ns^2np^3, in which the *ns*-orbital contains two paired up electrons while the *np*-orbitals contain three unpaired electrons in the np_x, np_y and np_z levels (See Vol. I. Chapter I). Thus, all of them are three short of the valence-shell electronic configuration of the next inert gas (*octet*). So, in principle, they can attain the *octet* structure (in their valence-shell) by several ways : (*a*) They may lose all the five valence-electrons and attain the octet of the preceding inert gas and thereby form the true +5 charged cations. But, this is energetically impossible and hence is ruled out completely. (*b*) The gaining of three electrons may lead to the formation of a true trinegative R^{3-} species. But, it is also an unfavourable process. [In practice, it is not achieved except in the most electronegative member, nitrogen.] (*c*) They may form of three covalent single bonds, in which the three unpaired *np*-electrons are involved, with the *ns*-electron-pair remaining as a *lone-pair* available for donation to acceptors like Lewis acids. The electronegativity of the other members of this group are much lower and hence they form mostly covalent compounds even with the most electronegative elements of Gr. VIB and VIIB. Even the chemistry of nitrogen is dominated by covalent compounds. It is to be noted that the compounds of bismuth are of predominantly ionic character which is quite expected. Thus, the ionic nature of the bonds in the trichlorides increase regularly from N – Cl to Bi – Cl.

Nitrogen being an element of low atomic number, its outermost level has $n=2$, for which no '*d*'-orbitals are available for bonding purposes and hence, it can form only tricovalent species. But, from phosphorus ($n=3$), *d*-orbitals are available for bonding purposes when such requirements arise, and P, As, Sb and Bi can expand their octet to form hexacovalent compounds.

Oxidation states : All the elements of this group display *formal** positive and negative oxidation states. Since the Gr. VB elements are closer to the succeeding inert gases, their chemisty is pervaded by negative oxidation states.

Negative oxidation states : As already discussed, the true -3 oxidation state is only achieved by nitrogen in the nitrides, while a formal -3 state is attained by the other elements in their compounds with highly electropositive elements such as in the hydrides. The stability of the -3 oxidation state decreases down the group, parallelling the decrease in electronegativity, with bismuth hardly exhibiting a negative oxidation state. This is the reason of the pronounced decrease in stability of the hydrides (RH_3) down the group from nitrogen to bismuth.

Positive oxidation states : The valence-shell configuration ns^2np^3 naturally suggests the existance of a *formal* $+3$ oxidation state, corresponding to the participation of the three *np*-electrons, and a

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* In a compound involving shared electron-pair bonds between two (or more) elements differing in electronegativity (e.g. HCl, H_2O, NF_3 etc.), electroneutrality principle is applied for assigning a *formal charge* or *oxidation number* or *oxidation state* to the atom of an element present in the molecule being considered. This formal charge on an element in a compound may be defined as the electrical charge (positive or negative) which it would carry, if the molecule is made up of ions only. The more electronegative element is assigned a negative formal charge, while the less electronegative one is assumed to carry positive charge. Thus, in HCl, the formal charge on hydrogen is $+1$ and that on chlorine is -1. Similarly, in H_2O, the formal charge on two hydrogens together is $+2$ and that on oxygen is -2. The terms *formal charge* and *oxidation state* are taken as synonimous here.

formal +5 oxidation state in which both the two *ns* and the three *np*-electrons take part in chemical bonding with a more electronegative element. The +3 oxidation state is the stablest and is most common, while the stability of the +5 oxidation state decreases down the group and becomes very unstable in bismuth. As is predicted by Fajan's rules of ionic distortion, the compounds in the +5 oxidation state are much more covalent in nature than the corresponding compounds in which they exist in the +3 state. In the +5 state, all these elements are predominantly non-metallic and acidic in nature. It is to be noted that nitrogen and phosphorus exhibit the oxidation states of +4, and +1, while nitrogen exhibits the +2 oxidation state also.

The positive and negative oxidation states exhibited by this group of elements are included in the following table along with relevant examples.

TABLE 16.2

Oxidation states of the Gr. VB elements :

Oxidn. State	Nitrogen	Phosphorus	Arsenic	Antimony	Bismuth
+5	N_2O_5 HNO_3	P_4O_{10} H_3PO_4 PCl_5	As_2O_5 H_3AsO_4 $AsCl_5$	Sb_2O_5 $HSb(OH)_6$ $SbCl_5$	Bi_2O_5 $NaBiO_3$
+4	NO_2 or N_2O_4	—	—	—	—
+3	N_2O_3 HNO_2 NCl_3	P_4O_6 H_3PO_3 PCl_3	As_4O_6 H_3AsO_3 $AsCl_3$	Sb_4O_6 H_3SbO_3 $SbCl_3$ $SbOCl$	Bi_2O_3 $BiCl_3$ $BiOCl$
+2	NO	—	—	—	—
+1	N_2O $H_2N_2O_2$ (hyponitrous acid)	H_3PO_2 (hypophosphorous acid)	—	—	—
0	N_2	P_4	As	Sb	Bi
−1	NH_2OH	—	—	—	—
−2	N_2H_4	P_2H_4	—	—	—
−3	NH_3 NH_4^+	PH_3 PH_4^+	AsH_3	SbH_3	BiH_3

The inert pair effect : The stability of the +5 oxidation state decreases with the increase in atomic number because of the increased reluctance of the two *ns*-electrons to take part in chemical bonding. This is termed the "*inert pair effect*". It becomes operative from antimony and is very high in bismuth. Hence, pentavalent antimony compounds are less stable than the corresponding trivalent compounds, while bismuth forms pentavalent compounds only with the highly electronegative element oxygen and even then, it is rather unstable. Such a pair of '*s*' electrons in the outermost quantum level are to be unpaired by supplying sufficient energy before they can participate in bonding. It is this amount of energy (required to '*unpair*' these two paired up *ns* electrons) that increases gradually from nitrogen to bismuth, and in bismuth it becomes so high that it can be supplied only in its reactions with oxygen, the energy of formation of Bi—O bonds being very high.

Catenation or self-linkage : Catenation or the tendency to form linkage among the atoms of the same element, which is the special characteristic of carbon and, to some limited extent, of silicon, is also noticed in nitrogen and phosphorus. Nitrogen compounds containing two self-linked nitrogens are found in hydrazine and its derivatives, in the azo compounds etc. Three self-linked nitrogens are present in the azides. Unstable compounds containing eight nitrogen atoms linked together have also been prepared. Four phosphorus atoms are self-linked in the P_4-molecule. However, that the N–N and P–P bonds are much more unstable than the C–C bond, is evident from the following bond-energy data :

N—N	20.0 Kcals/mole,
P—P	18.9 Kcals/mole,
C—C	58.6 Kcals/mole.

Electron donor characteristics : In the compounds of these elements in the tripositive oxidation state, the two *ns*-electrons are not involved in bonding and are called the *lone pair* of electrons. Such compounds exhibit a tendency to act as election-pair donors towards appropriate positively charged metal ions, forming co-ordinate covalent linkage (see Vol. I, page 289). Nitrogen compounds show greatest donor capacity which falls off rapidly with the increase in atomic number and decrease in electronegativity, and is totally absent in bismuth. Nitrogen shows maximum donor ability in the form of ammonia and its various derivatives. Among the halides of the general formula RX_3 (where R=N, P, As and X=F, Cl, Br, I), the donor capacity falls off as the electronegativity of the halogen increases. This is because of the increased attraction of the bond-pair of the R—X bond towards the halogen atom, which results in the much more tight binding of the lone pair on the R atom and makes the lone pair less available for co-ordination to an acceptor centre.

Chemical reactivity : Chemical reactivity of these elements do not show any regular variation with atomic number. Nitrogen, inspite of its highly electronegative character, is chemically rather unreactive. Only at very high temperatures, it combines with highly electropositive elements like Li, Mg, Ca and Al, forming the corresponding nitrides. It reacts with oxygen only at the very high temperatures (2500°C and above) produced by an electric arc and forms nitric oxide. This reaction is the basis of **fixation of nitrogen** by the Birkeland and Eyde Process and also for the fixation of nitrogen in the upper atmosphere under the influence of lightning discharge. The reason of this rather unexpected lack of reactivity of elemental nitrogen lies in the extreme stability of the nitrogen molecule, $N{\equiv}N$, as reflected in its high dissociation energy of 225.2 Kcals/mole.

White phosphorus is extremely reactive and reacts readily with oxygen, probably because the P—O bond is much more stable than the P—P bond present in elemental white phosphorus. The other forms of phosphorus are much less reactive for reasons to be discussed later.

As, Sb and Bi are unreactive and combines with oxygen, only on heating, to form their oxides.

None of the elements decompose water under ordinary conditions or even on boiling.

Combination with metals : All the members of Gr. VB combines with strongly electropositive metals. Nitrogen combines with Li,

TABLE 16.2

The more important properties of the hydrides of the Gr. VB elements.

Property	NH_3	PH_3	AsH_3	SbH_3	BiH_3
Thermal stability	Highly stable.	Less stable than NH_3. Decomposes at 400°C.	Less stable than PH_3. Decomposes at 230°C.	Unstable. Decomposes even at ordinary temperatures.	Very unstable. Has a transient existence.
Reducing action	Not a reducing agent under normal conditions.	A stronger reducing agent than NH_3.	Fairly strong reducing agent.	Strong reducing agent.	Strong reducing agent.
Basic character	Fairly strong base. Forms ammonium salts with strong and weak acids.	Much weaker basc. Forms phosphonium salts with strong acids only. $PH_3+HCl=PH_4Cl$	Not basic.	Not basic.	Not at all basic. Rather acidic.
Hydrogen bonding	Considerable hydrogen bonding present. This is manifested in its rather high B. P., high viscosity and high dielectric constant.	Practically no hydrogen bonding present.	No hydrogen bonding present.	No hydrogen boning plesent.	No hydrogen boning present.
Structure	Nitrogen is present in the sp^3-hybridised state, with the lone pair placed in one of the sp^3-hybrid orbitals. The ultimate structure is pyramidal due to the lone pair-bond pair repulsion.	Same as that of NH_3.	Same as that of NH_3.	Probably similar to the structure of NH_3.	Nothing is known about its structure.

Mg and Ca forming the nitrides Li_3N, Mg_3N_2 and Ca_3N_2. Phosphorus forms calcium phosphide, Ca_3P_2, while arsenic forms arsenides like sodium arsenide, Na_3As, and antimony yields antimonides like Zn_3Sb_2 ; bismuth is found to yield bimuthides, such as Mg_3Bi_2.

Hydrides : All the members of this group form hydrides of the general formula RH_3. The variation of some important properties of these hydrides with the change in atomic numbers are represented in the following manner :

(i) Ionic character.
(ii) Reducing character.
(iii) Acidic character.

$\xrightarrow{\text{Increases}}$

NH_3 PH_3 AsH_3 SbH_3 BiH_3

$\xleftarrow{\text{Increases}}$

(iv) Thermal stability.
(v) Hydrogen bonding
(vi) Chemical stability

In all these hydrides, the VB elements display their formal -3 oxidation state because hydrogen is more electropositive than all of them. All these hydrides are predominantly covalent with ionic character increasing from NH_3 to BiH_3.

Ammonia, NH_3, the hydride of nitrogen is distinctly basic and forms salts with both strong (NH_4Cl) and weak acids [$(NH_4)_2CO_3$]. Phosphine, PH_3, is much weakly basic than NH_3 and forms phosphonium halides, PH_4X, on reaction with strong acids like HCl, HBr etc. The basic character is almost non-existent in AsH_3, SbH_3 and BiH_3, decreasing in that order. The hydrides of P, As, Sb and Bi are strong reducing agents. The reducing character increases from P to Bi, and is due to the increase in electropositive character of the elements which parallels the decrease in stability of these hydrides. Hydrogen bonding characteristics decrease from NH_3 to BiH_3 as a result of gradual decrease in electronegativity in that direction.

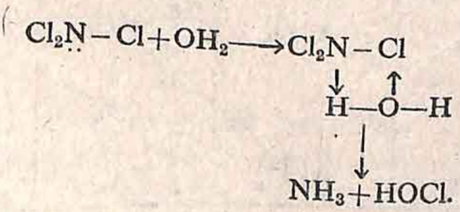
Halides : Two different types of halides, the trihalides (RX_3) and the pentahalides (RX_5), formed by the elements of this group are given below :

Elements	N	P	As	Sb	Bi
Trihalides	NF_3	PF_3	AsF_3	SbF_3	BiF_3
	NCl_3	PCl_3	$AsCl_3$	$SbCl_3$	$BiCl_3$
		PBr_3	$AsBr_3$	$SbBr_3$	$BiBr_3$
		PI_3	AsI_3	SbI_3	BiI_3
Pentahalides	—	PF_5	AsF_5	SbF_5	BiF_5
		PCl_5	$AsCl_5$	$SbCl_5$	
		PBr_5			

The trihalides : Except NBr_3 and NI_3, all the trihalides are well established. The trihalides are primarily covalent in nature, with ionic character increasing from nitrogen halides to the bismuth halides, due to the increase in electropositive character. All these halides have a tetrahedral or pyramidal structure, with the central element being present in an sp^3-hybrid state and the lone pair occupying one corner of the tetrahedron and inducing some pyramidal character due to considerable lone pair-bond pair repulsion (VSEPR theory, Vol. I. p. 148-49).

All the trihalides are hydrolysed in aqueous solution, excepting NF_3. The reason of hydrolytic stability of NF_3 and the lability of NCl_3 may be explained as follows : The first step of a hydrolytic reaction involves the formation of at least one extra bond of the reacting molecule with water molecules, involving either the central atom or the halide. In the case of NCl_3, Cl is capable of expanding its octet by utilising its 'd'-orbitals while N or F in NF_3 are incapable of doing so.

Thus, NCl_3 (and not NF_3) undergoes hydrolysis, and may be represented as :



$$Cl_2\ddot{N}-Cl+OH_2 \longrightarrow \begin{array}{c} Cl_2N-Cl \\ \downarrow \quad \uparrow \\ H-O-H \\ \downarrow \\ NH_3+HOCl. \end{array}$$

The trihalides of P, As, Sb and Bi undergo hydrolysis because all of them can use their d-orbitals to expand their octets. The hydrolytic reactions of the trihalides are given below :

$$\begin{aligned} NCl_3 &+ 3H_2O = NH_3 + 3HOCl \\ PCl_3 &+ 3H_2O \rightleftharpoons H_3PO_3 + 3HCl \\ AsCl_3 &+ 3H_2O \rightleftharpoons H_3AsO_3 + 3HCl \\ SbCl_3 &+ H_2O = SbOCl\downarrow + 2HCl \\ BiCl_3 &+ H_2O = BiOCl\downarrow + 2HCl \end{aligned}$$

Sb and Bi yield oxyhalids which are precipitated and contain the SbO^+ and BiO^+ ions. The oxo-cations are formed due to the highy acidic nature of the Sb^{+3} and Bi^{+3} cations which act with a water molecule as follows :

$$\begin{aligned} Sb^{+3} &+ H_2O = SbO^+ + 2H^+ \\ Bi^{+3} &+ H_2O = BiO^+ + 2H^+ \end{aligned}$$

The pentahalides : Nitrogen being a member of the first short period cannot use outer 'd' orbitals and hence cannot form pentahalides because of non-availability of required number of orbitals. But, all the subsequent elements can form five sp^3d^2 hybrid bonds (see Vol. I. p. 156-57) and form pentahalides mentioned before. These pentahalides possess a trigonal bipyramidal structure (*cf.* PCl_5 ; see Vol. I. p. 150).

They are completely hydrolysed in aqueous solution, yielding the corresponding highest oxyacids :

$$\begin{aligned} PCl_5 &+ 4H_2O = H_3PO_4 + 5HCl \\ AsCl_5 &+ 4H_2O = H_3AsO_4 + 5HCl \end{aligned}$$

Oxides : The formulae of the oxides formed by the Gr. VB elements are given in the following table :

Nitrogen	*Phosphorus*	*Arsenic*	*Antimony*	*Bismuth*
N_2O				
NO				
N_2O_3	P_4O_6	As_4O_6	Sb_4O_6	Bi_2O_3
NO_2 or N_2O_4				
N_2O_5	P_4O_{10}	As_2O_5	Sb_2O_5	Bi_2O_5

All the members of this group have oxides of the general formula R_2O_3 (the trioxides) and R_2O_5 (the pentoxides). Nitrogen forms the dioxide NO_2 or N_2O_4 and also the monoxide NO (known as nitric oxide) and another oxide, N_2O (nitrous oxide).

The trioxides of N, P and As, (N_2O_3, P_4O_6 and As_2O_3) are acidic, Sb_2O_3 is amphoteric, while Bi_2O_3 is distinctly basic. The trioxides of N, P and As gives the 'ous' acids on dissolution in water.

The pentoxides are all acidic, but the acidity decreases down the group from N_2O_5 to Bi_2O_5. The pentoxides are more strongly acidic than the corresponding trioxides because of the increase in positive oxidation state of the elements which make them stronger electron-acceptors and hence stronger Lewis acids. The pentoxides of N, P and As yield the corresponding 'ic.' acids on reaction with water.

Oxyacids : All the elements form oxyacids. The known acids of these elements are given below :

$H_2N_2O_2$ (hyponitrous)	H_3PO_2 (hypophosphorous) ($H_4P_2O_5$, pyrophosphorous)			
H_2NO_2	HPO_2 (meta phosphorous)			
HNO_2	H_3PO_3 $H_4P_2O_6$ (hypophosphoric)	H_3AsO_3		
HNO_3	H_3PO_4	H_3AsO_4	H_3SbO_4 Solid. Amphoteric, insoluble in water.	$HBiO_3$ Solid. Insoluble in water ; known as salts of strong alkalis like NaOH.
HNO_4 (pernitric)	H_3PO_5 or $H_4P_2O_8$ (perphosphoric) HPO_3 (meta) $H_4P_2O_7$ (pyro)			

The acid strengths of the 'ous' acids and the 'ic' acids decrease down the group with the increase in atomic number. Thus, HNO_3 is the strongest and $HBiO_3$ is the weakest oxyacid in the class of the 'io' acids. This is also due to the decrease in electronegativity in that direction so that, the ease of release of the proton of the HO– function of the oxyacid is decreased due to the decrease in electron withdrawing character of the central element, R, transmitted through the oxygen of the H→O→R group, to the electron-pair holding the hydrogen and the oxygen together. Again, the 'ic' acids are stronger than the corresponding 'ous' acids due to the increase in electronegativity of the central element due to its higher positive oxidation state and also due to the presence of a larger number of highly electronegative oxygen atoms. Thus, HNO_3 is much stronger than HNO_2, and H_3PO_4 is stronger than H_3PO_3.

Sulphides : Except nitrogen, all the other elements form sulphides. Electronegativity of nitrogen is higher than that of sulphur and hence, compounds of nitrogen and sulphur are better represented as sulphur nitrides. The known sulphides of P, As, Sb and Bi are :

	As_4S_4	Sb_2S_4	
P_4S_3	As_4S_6	Sb_2S_3	Bi_2S_3
P_4S_{10}	As_2S_5	Sb_2S_5	

The stability of the sulphides increases and their acidity decreases with the increase in atomic number due to the increase in electropositive character from N to Bi. Thus, the sulphides of P, As and Sb are soluble in ammonium polysulphide, but bismuth sulphide (which is basic) is not. This is the basis of separation of Gr. IIA and Gr IIB (of analytical chemistry) sulphides by treatment of the sulphide mixture (containing HgS, CuS, PbS, Bi_2S_3 CdS and As_2S_3, Sb_2S_3 and SnS) with yellow ammonium sulphide in which only As_2S_3, Sb_2S_3 and SnS_2 dissolve, forming the corresponding thio-salts.

THE INDIVIDUAL ELEMENTS OF Gr. VB.

NITROGEN.

As already noted at the begining of this chapter, about 80% of the atmospheric air is elemental nitrogen. In the combined state, it occurs mostly as nitrate in sodium and potassium nitrates. Coal, on distillation, yields ammonia and hence is an important source of nitrogen. It is an essential constituent of all kinds of living matter, being present as proteins containg appoximately 16% nitrogen.

Special characteristics of nitrogen.

As the first member of a periodic group (VB), nitrogen differs considerably from the other elements of this group. The reason underlying such differences are :

(i) Small size and high electronegativity.

(ii) Non-availability of '*d*'-orbitals for the expansion of its octet due to its low atomic number.

(iii) The extreme stability of the $N \equiv N$ linkage.

(iv) Extensive participation in hydrogen bonding due to its very high electronegativity.

For all practical purposes, nitrogen is obtained from air (by fractional evaporation of liquid air) and all the methods leading to its preparation from nitrogeneous compounds are almost of no practical utility. However, the following methods may be just mentioned :

1. **Nitrogen from ammonium nitrite :** On heating a mixture of sodium nitrite and ammonium chloride, ammonium nitrite is produced *in situ* which, being thermally unstable, decomposes into nitrogen and water :

$$NH_4Cl + NaNO_2 = NH_4NO_2 + NaCl \,;$$
$$NH_4NO_2 = N_2 \uparrow + 2H_2O.$$

This method is used for the preparation of nitrogen in the laboratory, where the issuing gas is collected by the downward displacement of water.

2. **Nitrogen from ammonia or an organic compound containing nitrogen :** On heating a mixture of an organic compound and CuO in a combustion tube, or by passing ammonia over heated CuO, nitrogen is set free :

$$2NH_3 + 3CuO = N_2 + 3H_2O + 3Cu.$$

It is better to allow the issuing gas to pass over a red-hot Cu-gauge, when any trace of N_2O, that many be formed, is reduced to nitrogen :

$$N_2O + Cu = CuO + N_2$$

This is the basis of estimation of nitrogen by Dumas method, the combustion being done in a current of CO_2 (which drives the liberated N_2 out of the combustion tube) and N_2 is collected over 50% KOH soln. in a nitrometer. KOH absorbs all CO_2, leaving free nitrogen.

Nitrogen from air : Atomospheric air is first purified and then liquified by standard processes. The liquid air is then subjected to fractional distillation, when the more volatile nitrogen (b.p. $-196°$) distils over first (for details see p. 314–316, Volume I).

Physical properties : Nitrogen is a colourless, odourless and tasteless gas, which is neither combustible nor a supporter of combustion. It does not help respiration, but is not poisonous. It is liquified below $-195.7°C$ and solidifies below $-209.9°C$. Nitrogen consists of two isotopes N^{14} and N^{15}, the ratio of $N^{14} : N^{15}$ being ≈ 272. The N^{15} isotope is frequently used as a tracer.

Chemical properties : Nitrogen is a diatomic gas which is rather inert in character. The inter-nuclear distance in the nitrogen molecule (N_2), is 1.095Å and it has a triple bonded structure :

$$:N\vdots\vdots N: \quad \text{or} \quad :N\equiv N:$$

The heat of dissociation of the nitrogen molecule is very high : $N_2(g) \rightleftharpoons 2N(g)$, $\triangle = 225.8$ Kcals/mole.

Even at 3000°C, the extent of dissociation is small. This indicates the extreme stability of the nitrogen molecule and is the main reason of its lack of pronounced chemical reactivity.

Active nitrogen : As already stated, elemental nitrogen is comparatively inert. However, an active variety of nitrogen is produced by passing electric discharge through gaseous nitrogen at low pressures. This so-called *active nitrogen* is highly reactive and reacts with several elements, forming unusual products. Thus, it reacts with hydrocarbons and produces HCN. It reacts with mercury and phosphorus, arsenic and sodium vapours, producing the corresponding nitrides.

The actual nature of *active nitrogen* is not known with certainty. It has been established that it contains some atomic nitrogen existing in an *excited* or *activated* state. After the stoppage of electric discharge, a yellow glow is observed which is probably due to the de-excitation of the active atomic nitrogen and their recombination into nitrogen molecules.

Reaction of nitrogen with different types of elements : Though much less reactive than the other gaseous elements like hydrogen, oxygen and the first two halogens, nitrogen is not totally inert, and combines with several elements under suitable conditions.

NITRIDES.

Nitrides are the binary compounds of nitrogen with elements of less electronegative character than nitrogen itself. Thus, nitrogen forms nitrides with the strongly electropositive metals, with some of the transition metals and with non-metals like B, C, P, and S and of course, with hydrogn. The nitrides may also be visualised as the derivatives of ammonia where all the hydrogen are replaced by metals or other elements of greater electropositive character than nitrogen.

Classification of nitrides : The properties of the nitrides vary widely and are largely influenced by the nature of the linkage between the metal (or non-metal) and nitrogen, which is governed by the nature of that metal or non-metal present in combination with nitrogen. Depending on their properties, the nitrides are classified, just like the hydrides, into (i) ionic, (ii) covalent and (iii) interstitial or metallic nitrides.

(i) **Ionic nitrides :** These nitrides contains the N^{3-} ion and are formed by lithium and copper (I) of group I and by all the members of group II of the Periodic Table. The general method of preparation of these nitrides is the direct combination of nitrogen and the metal at high temperatures :

$$6Li+N_2 \xrightarrow{250°C} 2Li_3N\ ;$$

$$3M+N_2 \xrightarrow{\sim 500°C} M_3N_2 \qquad [M=Mg,\ Ca,\ Sr,\ Ba].$$

The ionic nitrides are crystalline ionic solids with high melting points. They are hydrolysed by water, forming the metal hydroxide and liberating ammonia :

$$Li_3N+3H_2O=3LiOH+NH_3(g)\ ;$$

$$M_3N_2+6H_2O=3M(OH)_2+2NH_3(g)$$

$$[M=Mg,\ Ca,\ Sr,\ Ba].$$

Some more important reactions of ionic nitrides, represented by magnesium nitride, are given in fig. 16·1.

(ii) **Covalent nitrides :** The covalent nitrides include the volatile nitrides of the non-metals like hydrogen, carbon, silicon, phosphorus, sulphur etc. and the non-volatile nitrides of boron and aluminium.

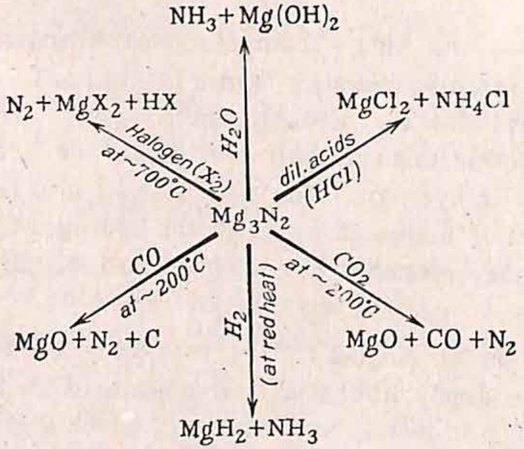


Fig. 16·1

The more general methods for the preparation of the covalent nitrides include the following :

(*a*) By heating of the amides,

$$B(NH_2)_3 \xrightarrow{\text{heat}} BN + 2NH_3(g),.$$

$$SiCl_4 \xrightarrow{NH_3} Si(NH_2)_4 \xrightarrow{\text{heat}} Si_3N_4.$$

(*b*) By heating the oxides of the elements with carbon in an atmosphere of nitrogen,

$$Al_2O_3 + 3C + N_2 \rightarrow 2AlN + 3CO.$$

(*c*) By heating the metal in a current of NO,

$$5B + 3NO \rightarrow B_2O_3 + 3BN.$$

All these nitrides are covalent in character and are usually monomeric in nature. The Gr. IIIA nitrides, BN and AlN, are giant molecules, with structures comparable to those of different forms of carbon, which arise out of the fact that one Gr. III atom and one Gr. V atom together are equivalent to two Gr. IV atoms. Thus, boron nitride, BN, exists in two forms structurally similar to graphite and diamond. The *graphite form* of boron nitride is sometimes called *inorganic graphite*. It is made up of layers of planar hexagonal units made up of alternate boron and nitrogen atoms, B – N bond-length being 1.45Å. Two adjacent layers or sheets are situated 3.34Å apart and are held together by van der Waal's forces. The *diamond form* of boron nitride has a structure analogous to diamond and is one of the hardest substances, harder even than diamond itself.

(iii) **Interstitial nitrides :** These nitrides are formed by the direct reaction of nitrogen with finely divided transition metals at 1100°–1200°C temperature. They include nitrides of the type MN, where M is a transition metal of Grs. IIIA, IVA and VA. Some examples are ScN, LaN, TiN, ZrN etc. Some other nitrides like W_2N, Mo_2N, Mn_4N and Fe_4N are also known. In these interstitial nitrides, the nitrogen atoms are contained in the interstices of the metallic lattice. All these nitrides resemble the interstitial carbides, and are very hard, with high melting points and exhibit good electrical conductivity. The interstitial nitrides are chemically inert and deviate from normal stoichiometry.

HYDRIDES : AMMONIA (NH_3)—Manufacture on a large scale.

Large scale manufacture of ammonia is mostly done by the Haber's process. This process is based on the direct combination between the elements hydrogen and nitrogen according to the following equation :

$$\underset{\text{1 vol.}}{N_2} + \underset{\text{3 vols.}}{3H_2} \rightleftharpoons \underset{\text{2 vols.}}{2NH_3}\ ; \quad \Delta H = -12.2 \text{ Kcals/mole.}$$

This is a *reversible* and *exothermic* reaction, in which contraction in volume takes place due to the forward reaction.

Physico-chemical principles underlying this process of manufacturing ammonia can be clearly understood by applying the **Le Chatelier's principle of labile equilibrium**, which states that, *whenever a system at equilibrium is subjected to a stress* (such as change in pressure, temperature and concentration), *it reacts in a direction which tends to relieve itself of that stress.*

Effect of temperature on the synthesis of ammonia : Since this reaction is an exothermic one, the yield of ammonia would increase at lower temperatures. However, the rate of a reaction is primarily dependent on the temperature of the reaction and, on an average, the rate of a reaction is nearly doubled by a 10°C rise of the reaction-temperature. In industry, not only the yield but also the time required to reach the equilibrium is of great importance. At a very low temperature, the yield will be high but, at the same time, the time involved will be very long, which is not economical in industrial processes. Thus, it is essential to strike a balance between the loss in yield and gain in the time-element, and for every exothermic reaction utilised for large scale manufacture, there is an *optimum temperature*, around which it can be worked profitably.

Influence of a catalyst : It is well known that a suitable catalyst is capable of tremendously influencing the speed of a chemical reaction, but it cannot alter the position of the equilibrium. Hence, a catalyst can take care of the time-element involved in a reaction. Thus, the optimum temperature of an exothermic reaction will depend on the efficiency of the catalyst being used. For Haber's process of ammonia synthesis, the catalyst used is an iron catalyst promoted with molybdenum or oxides of potassium and aluminium. The optimum temperature for this reaction is 550°C.

Influence of pressure : Since this reaction involves a decrease in volume (4 vols. to 2 vols.), it is quite evident that an increase of pressure will increase the yield. The table given below represents the variation of yield of ammonia with pressure and temperature :

Percent yield of ammonia at different temperatures and pressures.

Temp. (°C)	Pressure in atmospheres					
	10	50	100	300	600	1000
	14.73%	39.41%	52.04%	70.96%	84.21	92.55
300	3.85 ,,	15.27 ,,	25.12 ,,	47.00 ,,	65.20	79.82
400	2.10 ,,	9.78 ,,	16.50 ,,	36.00 ,,	54.00	69.80
450	1.21 ,,	5.56 ,,	10.61 ,,	26.44 ,,	42.15	57.47
500	0.76 ,,	4.21 ,,	6.80 ,,	19.00 ,,	32.00	41.20
600	0.49 ,,	2.26 ,,	4.52 ,,	13.77 ,,	23.10	31.43
700	0.23 ,,	1.05 ,,	2.18 ,,	7.28	12.60	12.87

In Haber's process, the pressure employed is 200 atmospheres, and though a higher pressure could have increased the yield considerably, the above pressure is quite adequate from economic point of view. The use of higher pressure involves serious technical problems and sharp increase in expenditure.

Actual process of manufacture of ammonia.

(a) Raw materials : The raw materials used in this process are : Pure and dry (i) hydrogen and (ii) nitrogen. Hydrogen is obtained by (a) electrolysis of water (where cheap electricity is available), (b) by the steam-iron process in which steam is passed over red-hot iron, or (c) from water gas. Nitrogen is obtained by (a) fractional evaporation of liquid air, or (b) from producer gas.

At Sindri, the largest ammonia manufacturing unit in our country, the raw materials, N_2 and H_2, are obtained by the **Bosch process** using coke, air and water. The H_2 and N_2 produced, (after drying) are converted into NH_3 by the Haber process and hence, this Indian process of manufacture of NH_3 gas goes by the name **Haber-Bosch process.**

Water gas $(CO+H_2)$ is produced by the action of steam on red hot coke (see vol. II p. 50). Producer gas $(CO+N_2)$, generated by passing air over red-hot coke, is mixed with water gas in required proportions and the mixture, along with excess steam, is passed through a chamber containing the heated catalyst at 450°C. This catalyst is a mixture of Fe_2O_3 and Cr_2O_3, and its function is to oxidise CO to CO_2 by the reaction, $CO+H_2O=CO_2+H_2$, whereby hydrogen is produced from steam. The issuing gases, containing N_2, H_2, CO_2 and traces of CO, are first passed through towers containing water at high pressure, where CO_2 is absorbed. It is then passed through ammoniacal cuprous formate solution under 200 atmospheres, when the last traces of CO are removed. **The gas-mixture comming out contains pure N_2 and H_2 in 1 : 3 ratio** and are dried by passing through soda-lime chambers. This is known as the *synthesis gas.*

(b) **Synthesis of NH_3 from N_2 and H_2 :** The above gas-mixture is compressed to 200 atmospheric pressure by compression pumps and is fed into the tubular catalyst chamber or reactor made of *chrome-vanadium steel*, fitted with perforated trays or shelves containing the catalyst and promoters. The catalyst chamber is electrically preheated to a temperature of 550°C (optimum temperature). The synthesis gas is first circulated around the catalyst chamber kept at 550°C, whereby it attains the temperature of the catalyst chamber, and is then passed through the catalyst when the reaction, $N_2+3H_2 \rightleftharpoons 2NH_3$, takes place, producing about 12% ammonia. This mixture, containing NH_3 and unreacted N_2 and H_2, is then allowed to pass out for the collection of NH_3 and more synthesis gas is pumped into the catalyst chamber.

Once the reaction is started, no external heating is necessary, the heat of reaction maintains the required temperature in the catalyst chamber.

The gases coming out of the catalyst chamber (containing 12% NH_3 and the rest unconverted N_2 and H_2) are passed through cooling coils and then either (i) liquified by the application of pressure to yield liquid ammonia, or (ii) absorbed in water, producing concentrated aqueous solution of ammonia, which is commercially called *liquor ammonia*.

The unreacted hydrogen and nitrogen are not affected by any of the above two procedures, and are passed through driers, mixed with fresh nitrogen and hydrogen, compressed to 200 atmospheres and re-cycled. This makes the production of ammonia a continuous process.

Other methods of obtaining ammonia on large scale.

(a) Ammonia is also manufactured by the **cyanamide process.** In the first step, calcium carbide (CaC_2) is prepared by reacting coke with quicklime, CaO, (obtained by the calcination of limestone, $CaCO_3$) in an electric arc furnace at 2100 – 2200°C :

$$\underset{\text{limestone}}{CaCO_3} \xrightarrow{\text{heat}} \underset{\text{quicklime}}{CaO}+CO_2$$

$$CaO+3C \rightarrow \underset{\text{calcium carbide}}{CaC_2+CO}$$

The calcium carbide is then cooled to ~ 1100°C and nitrogen is passed through it, when CaC_2 reacts with nitrogen, forming calcium cyanamide and free carbon : $CaC_2+N_2=CaCN_2+C$.

The grey mass obtained is known as *nitrolim*. Any unconverted CaC_2 is decomposed with water in order to prevent ammonia being contaminated with acetylene.

Calcium cyanamide is then hydrolysed with superheated steam at 110°—115°C under 5—7 atmospheric pressure, when ammonia and calcium carbonate are produced. The hydrolysis reaction is exothermic in nature.

$$CaCN_2+3H_2O=2NH_3+CaCO_3+\text{heat.}$$

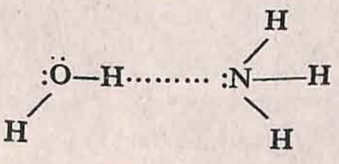
This method of manufacture of ammonia is not used at present, but nitrolim is still used directly as a fertilizer.

(b) **Ammonia as a bye-product of destructive distillation of coal.** During the manufacture of coal gas from *bituminous coal* by its destructive distillation, the aqueous distillate, collected along with the coal tar, contains considerable amount of ammonia. Steam is passed through this aqueous solution, when most of the NH_3 comes off with the steam. The residual solution is then heated with milk of lime to drive out the remaining ammonia. Ammonia produced in this method is generally absorbed in 60% sulphuric acid to produce ammonium sulphate solution :

$$2NH_3+H_2SO_4=(NH_4)_2SO_4.$$

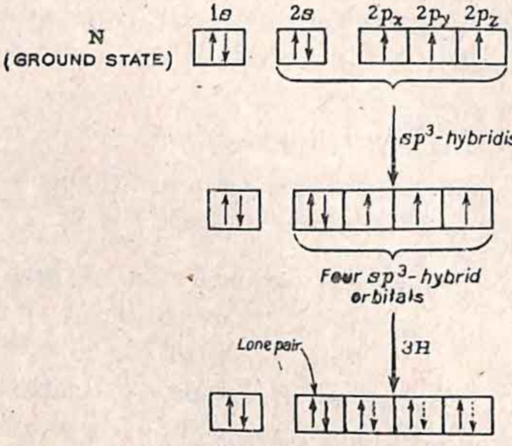
This is then evaporated to crystallisation and is widely used as a nitrogenous fertiliser.

Properties of ammonia : Ammonia is a colourless gas, lighter than air and possesses a characteristic pungent smell. As its critical temperature is rather high (32.5°C), it is easily liquified by the application of pressure alone. The b.p. of liquid ammonia is −33°C and the liquid freezes at −77.8°C to a crystalline white solid. It is extremely soluble in water (at 0°C, 1 vol. of water dissolves 1175 vols. of ammonia). In aqueous solution, ammonia is present in the hydrated state, with the water molecules linked to the ammonia molecule through hydrogen bonding,



Structure of the ammonia molecule.

Ammonia is a covalent compound, and it has been found experimentally that it has a pyramidal structure, in which the H—N—H bond angle is 107°. This structure of ammonia, treated as a AX_3 type molecule, has been given in vol. I, Chapter III, p. 148-49, under the discussion on VSEPR theory. It can also be explained using the principle of orbital hybridisation (Fig. 16·2). The dotted arrows represent the electrons supplied by the hydrogen atoms. As we have seen in the case of sp^3-hybridised carbon, the H—N—H angles should be 109°28′, and the molecule is tetrahedral. However, the actual structure of the ammonia molecules assumes pyramidal nature due to lone-pair-bond-pair repulsion.

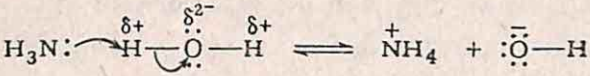


(The dotted arrows represent the electrons supplied by the hydrogen atoms)

Fig. 16·2

Basic character of ammonia : The structure of ammonia, discussed just now, clearly indicates *its inherent basic character, because of the presence of a lone-pair of electrons* in one of the sp^3-hybrid orbitals, which it can easily donate to an electron-pair acceptor or Lewis acid (see Chapter III p. 223). Again, since the capacity of donating one or more lone-pairs to a suitable acceptor (a metal ion M^{+n}) determines the capacity of a donor for complex formation, ammonia can act as a good *neutral monodentate* ligand molecule (see vol. I, p. 280). Thus, ammonia forms a large number of complexes with transition and non-transition metal ions, known as the *ammine complexes* (See Table 7.2., vol. I, p. 284).

Since the NH_3 molecule is a stronger Lewis base than the water molecule, in aqueous solution it undergoes the acid-base reaction :



$$H_3N\!: + \overset{\delta+}{H}-\overset{\delta^{2-}}{\ddot{O}}-\overset{\delta+}{H} \rightleftharpoons \overset{+}{N}H_4 + :\overset{-}{\ddot{O}}-H$$

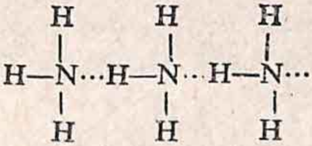
However, as ammonia is a rather weak base, this equilibrium is predominantly displaced towards the left.

The basic character of ammonia in water solution is due to the generation of $:\ddot{O}H^-$ ions as shown just now. This is clearly indicated by the precipitation of the hydroxides of many metals from the aqueous solution of their salts by the addition of aqueous ammonia or passing ammonia gas through the solutions.

$$MCl_3 + 3NH_3 + 3H_2O \rightarrow M(OH)_3 \downarrow + 3NH_4Cl,$$
$$\text{where } M = Al^{+3}, Cr^{+3}, Fe^{+3} \text{ etc.}$$

Hydrogen bonding in liquid ammonia.

Being one of the most electro-negative elements in the Periodic Table, nitrogen participates in hydrogen bonding (See Ch. III, vol. I, p. 175), leading to molecular association in the liquid state, which may be represented as :



$$H-\underset{H}{\overset{H}{N}}\cdots H-\underset{H}{\overset{H}{N}}\cdots H-\underset{H}{\overset{H}{N}}\cdots$$

This increase in *effective molecular weight* of ammonia in the liquid state is the reason for its higher m.p., b.p., surface tension, viscosity, dielectric constant etc. in relation to the comparable hydrides (PH_3, AsH_3 and SbH_3) of the other members of this group, in which there can be no hydrogen bonding due to less electro-negative character of the central elements.

Reducing character : Ammonia is not a good reducing agent, because in the N—H bond, the hydrogen end is positive and hence, when this bond is broken, hydrogen will not generally be liberated as H^- or even as H·-atom, which are the actual reducing agents. But, in the case of the hydrides of the heavier members (M) of this group, the M—H bond is either purely covalent or ionic, with slight negative charge accumulating on the hydrogen end and hence, they are reducing in character.

Laboratory method of preparation of ammonia.

Ammonia is prepared in the laboratory by heating an ammonium salt *with a base stronger than ammonia itself*: $NH_4X + OH^- \rightarrow NH_3 + H_2O + X^-$. This is a case of the stronger Lewis base OH^- displacing the weaker NH_3 from its compound. Generally, slaked lime is used as the base and NH_4Cl as the ammonium salt: $2NH_4Cl + Ca(OH)_2 = 2NH_3 + CaCl_2 + 2H_2O$.

Liquid ammonia and some of its special characteristics.

As already described in the process of manufacture of ammonia by the Haber-Bosch process, liquid ammonia is obtained by the application of pressure on NH_3 gas, keeping the temperature below the critical temperature (32.5°C).

Liquid ammonia has a rather high dielectric constant like water and hence, is capable of overcoming the forces of electrostatic attraction holding together the cations and the anions in the crystal lattice of ionic compounds or electrolytes. Thus, it dissolves many salts like halides, cyanides, thiocyanates, nitrates, nitrites etc. and the solutions conduct electricity. The role of ammonia as a medium for the acid-base reactions have been discussed in the chapter on acids and bases under the item "solvent-system concept" (vol. I, p. 219).

Solution of some metals in liquid ammonia.

Unlike water, liquid ammonia is capable of dissolving strongly reducing metals (like the alkali and the alkaline earths) without chemical reaction. Thus, alkali metals readily dissolve in liquid ammonia, producing blue solutions with strong reducing property. On evaporation of these solutions, the metals can be recovered. The solubility of the alkaline earth metals (Mg; Ca, Sr etc.) are less than that of the alkali metals, and the solid obtained by evaporation of ammonia consists of the unstable metal ammoniates, $M(NH_3)_6$. These solutions conduct electricity, which is attributed to the presence of mobile *ammoniated electrons* generated due to the existence of the following equilibrium processes:

$$M \rightleftharpoons M^+ + e^-$$

$$M^+ + xNH_3 \rightleftharpoons M(NH_3)_x{}^+$$

$$e^- + yNH_3 \rightleftharpoons e^-(NH_3)_y$$

This can explain both the conductance and the reducing character of such solutions. It has also been found that the anion is the same, even when different metals are dissolved in liquid ammonia.

Non-metals like phosphorus, sulphur and selenium are also soluble in liquid ammonia to some extent and their solubility may be attributed to their reactions with the solvent.

Uses of ammonia : (*a*) Liquid ammonia is widely used in refrigeration because of its large heat of evaporation.

(*b*) Ammonia is used for the manufacture of nitrogenous and phosphatic fertilizers in the form of ammonium sulphate, ammonium nitrate, calcium ammonium nitrate, ammoniated superphosphate etc. NH_4Cl is largely used in the manufacture of *dry cells*. Ammonia itself is used in the manufacture of soda ash by the Solvay process. Ammonium salts are also used in medicine, and NH_4NO_3 in explosives.

(*c*) It is also used as a ready source of hydrogen. As ammonia contains $1\frac{1}{2}$ times it own volume of nitrogen, the catalytic decomposition of ammonia generates large volume of hydrogen which is used for welding by oxy-hydrogen torch.

(*d*) As an aqueous solution (in which NH_3 exists as NH_4OH), it is used as a reagent in both qualitative and quantitative analysis.

SALTS OF AMMONIA WITH ACIDS—THE AMMONIUM SALTS.

Since ammonia is fairly basic, containing one lone-pair of electrons, it reacts with protonic acids, leading to the formation of ammonium salts (see vol. I. p. 224).

$$NH_3+HX=NH_4X,$$
$$(X=Cl, Br, I, NO_3, NO_2 \text{ etc.}).$$
$$2NH_3+H_2SO_4=(NH_4)_2SO_4\,;$$
$$2NH_3+CO_2+H_2O=(NH_4)_2CO_3.$$

Ammonium sulphate and ammonium nitrate (along with urea, calcium nitrate and nitrolim) find wide use in agriculture as nitrogenous fertilizers.

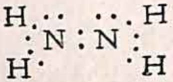
Manufacture of ammonium sulphate : If sulphuric acid is easily available, gaseous ammonia is passed into the acid and the resultant solution of ammonium sulphate is evaporated to crystallisation to prepare $(NH_4)_2SO_4$ on a large scale.

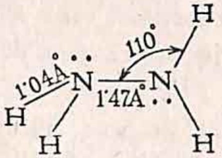
It reduces Fehling's solution, producing cuprous oxide :

$$4Cu^{++}+NH_2.NH_2 \rightarrow 4Cu^{+}+4H^{+}+N_2.$$

Uses : Hydrazine is used as a rocket fuel. It is widely used in organic chemistry as a reagent and also in pharmaceutical industry to synthesise various derivatives of hydrazine used as antituberculosis drugs, blood pressure depressants and nerve-soothing drugs.

Structure : The structure of hydrazine is similar to that of hydrogen peroxide, which may be represented as :





Hydrazoic acid, HN_3 : Hydrazoic acid is best prepared from its sodium salt, which is obtained in 90% yield by the action of nitrous oxide on sodamide at 190°C :

$$2NaNH_2+N_2O=NaN_3+NaOH+NH_3,$$

the completion of the reaction being indicated by the stoppage of ammonia evolution. The resultant mass is cooled and distilled with dilute sulphuric acid to produce dilute hydrazoic acid. This is again distilled in presence of fused calcium chloride to yield anhydrous HN_3.

Pure hydrazoic acid is a colourless liquid, boiling at 37°C and melting at -80°C. It is extremely toxic and highly explosive, decomposing into the elements with the evolution of considerable heat : $2HN_3=3N_2+H_2$; ($\Delta H=-123$ Kcals/mole.)

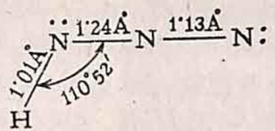
It is a weak acid ($K_a \sim 10^{-5}$) and forms many metallic salts. The heavy metal azides like lead, barium and mercury azides are highly explosive and are used as detonators. The azide ion, N_3^-, exhibits similarity to the halide ions and is recognised as a *pseudohalide*. The hydrazoic acid and its salts are not good reducing agents and are oxidised only by strong oxidising agents like $KMnO_4$ and ceric salts. Oxidation with ceric salts is quantitative and is utilised for the estimation of azides :

$$2Ce^{+4}+2N_3^-=2Ce^{+3}+3N_2.$$

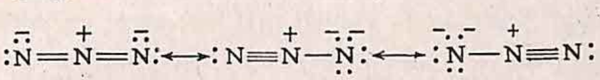
Reaction with iodine is also quantitative in presence of a catalyst like thiosulphate or sulphide : $I_2+2HN_3=2HI+3N_2$.

Structure : Hydrazoic acid has a bent structure with the **H-N-N** angle of 110°52′ and the three nitrogens arranged in a linear fashion :

$\mathrm{H\!:\!\ddot{N}\!::\!N\vdots\vdots N\!:}$ $\quad$ $\mathrm{H-\ddot{N}=N\equiv N\!:}$



However, the azide ion, N_3^-, is found to have a symmetrical linear structure and is best represented as a resonance hybrid of the following type :



$$:\overset{-}{\ddot{N}}=\overset{+}{N}=\overset{-}{\ddot{N}}: \longleftrightarrow :N\equiv\overset{+}{N}-\overset{-\,-}{\underset{\cdot\cdot}{\ddot{N}}}: \longleftrightarrow :\overset{-\,-}{\underset{\cdot\cdot}{\ddot{N}}}-\overset{+}{N}\equiv N:$$

Uses of hydrazoic acid : As salts of heavy metals [e.g. lead azide, $Pb(N_3)_2$], it is used as detonators in high explosives.

Hydroxylamine, NH_2OH : This may be considered as a derivative of ammonia, where one hydrogen is replaced by an OH group.

Preparation : This is generally prepared by the controlled reduction of a nitrite by sulphur dioxide, when hydroxyl amine sodium sulphonate is formed which, on hydrolysis, yields hydroxylamine.

A concentrated solution of sodium nitrite (1 mole) is mixed with a concentrated solution of sodium carbonate (3 moles). The mixture is cooled in ice and SO_2 gas is passed through it until the solution becomes just acidic. The temperature of the reaction-mixture is always kept below 0°C. Hydroxylamine is formed according to the following reactions :

$$NO_2^- + HSO_3^- \rightarrow \underset{\substack{\text{nitroso}\\ \text{sulphonic acid}}}{HO_3SNO} \xrightarrow{HSO_3^-} \underset{\substack{\text{nitroso}\\ \text{disulphonic acid}}}{(HO_3S)_2NOH} \xrightarrow{HCl} \underset{\substack{\text{hydroxylamine}\\ \text{hydrochloride}}}{NH_2OH.HCl}$$

The solution of $NH_2OH.HCl$, containing H_2SO_4 generated by the hydrolysis of $(HO_3S)_2NOH$, is first treated with $BaCl_2$ solution to remove the sulphate. It is then evaporated and the residue is extracted with alcohol, in which $NH_2OH.HCl$ is highly soluble. This solution yields crystals of $NH_2OH.HCl$ on evaporation. Free hydroxylamine can be generated easily by treating the methanolic solution of $NH_2OH.HCl$ with calculated quantity of KOH in methanol and filtering off the precipitated KCl.

Properties : The pure compound is a colourless liquid, decomposing spontaneously above 0°C. Because of such unstable character in the pure state, it is generally handled as the solid salt, hydroxylamine hydrochloride. However, its aqueous solutions of less than 60% concentration are fairly stable. Above 15°C, it decomposes spontaneously into a mixture containing water, ammonia, nitrous oxide and nitrogen.

It is a monoacidic base, weaker than ammonia, and forms salts with strong protonic acids like HCl, H_2SO_4 etc. Its basic character is also manifested in the formation of co-ordination complexes in which it acts as a monodentate ligand, donating the lone-pair on the nitrogen atom.

Hydroxylamine behaves both as an oxidising and a reducing agent. This is probably because of the fact that it may be considered to be derived from H_2O_2 by the replacement of one O-H by an $-NH_2$ group, or from NH_3 by the replacement of one H-atom by an O-H group.

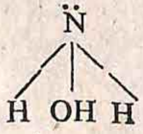
In neutral or acid solutions, hydroxylamine reduces ferric to ferrous and cupric to cuprous, itself being oxidised to N_2O in the process :

$$4FeCl_3+2NH_2OH=4FeCl_2+N_2O+4HCl+H_2O\ ;$$
$$4CuO+2NH_2OH=2Cu_2O+N_2O+3H_2O.$$

But, in alkaline solution, hydroxylamine oxidises ferrous hydroxide to the ferric state, itself being reduced to ammonia :

$$2Fe(OH)_2+NH_2OH+H_2O\rightarrow 2Fe(OH)_3+NH_3.$$

Structure : The structure of hydroxylamine follows from the structure of ammonia, with one hydrogen atom replaced by an OH group, i.e. it has a more or less pyramidal structure :



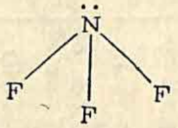
Uses of hydroxylamine : It is generally used (as its hydrochloride) as a reagent in organic synthesis and as a reducing agent.

Halides of nitrogen : Apart from various mixed halides reported from time to time, NF_3 and NCl_3 are the two stable and well-established halides of nitrogen. NBr_3 is also formed by the reaction of bromine on ammonia at pH less than 6. But, it is very unstable. When iodine is dissolved in concentrated ammonia, an unstable black compound of composition $NI_3.NH_3$ is said to be formed. Nitrogen does not form any pentahalide due to the absence of suitable *d*-orbitals.

Nitrogen trifluoride, NF_3 : This is conveniently obtained by the electrolysis of fused ammonium bifluoride, NH_4HF_2, at 125°C. The issuing gas is passed through polythene U-tubes containing solid KF (to remove HF), solid MnO_2 (to convert ozone to oxygen) and chilled below $-119°C$, when NF_3 is obtained as a liquid. This is distilled for purification.

NF_3 is a colourless gas boiling at $-119°C$ and freezing at $-217°C$. It is the stablest of all nitrogen halides and is not explosive. It is not hydrolysed by water or alkalis. It does not attack mercury, nor reacts with glass.

It is a covalent compound and hence, its dipole moment is very small because of the non-polar character of each N—F bond. It has a distorted tetrahedral structure similar to that of NH_3.

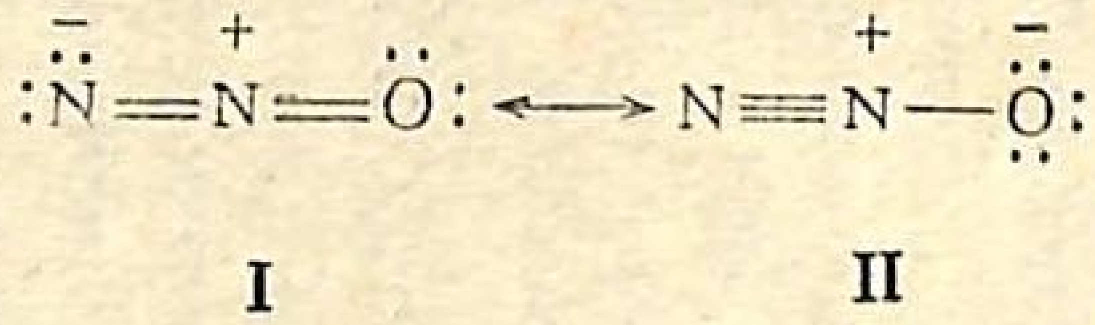
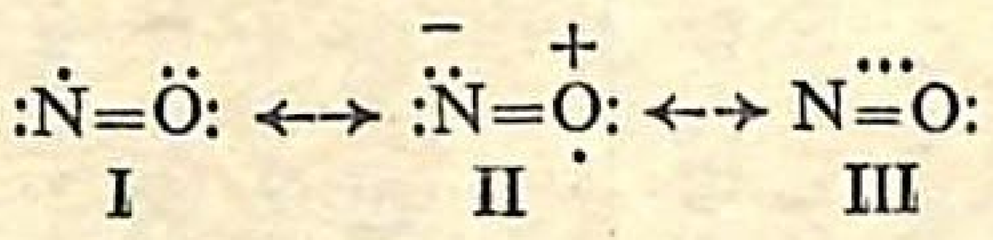
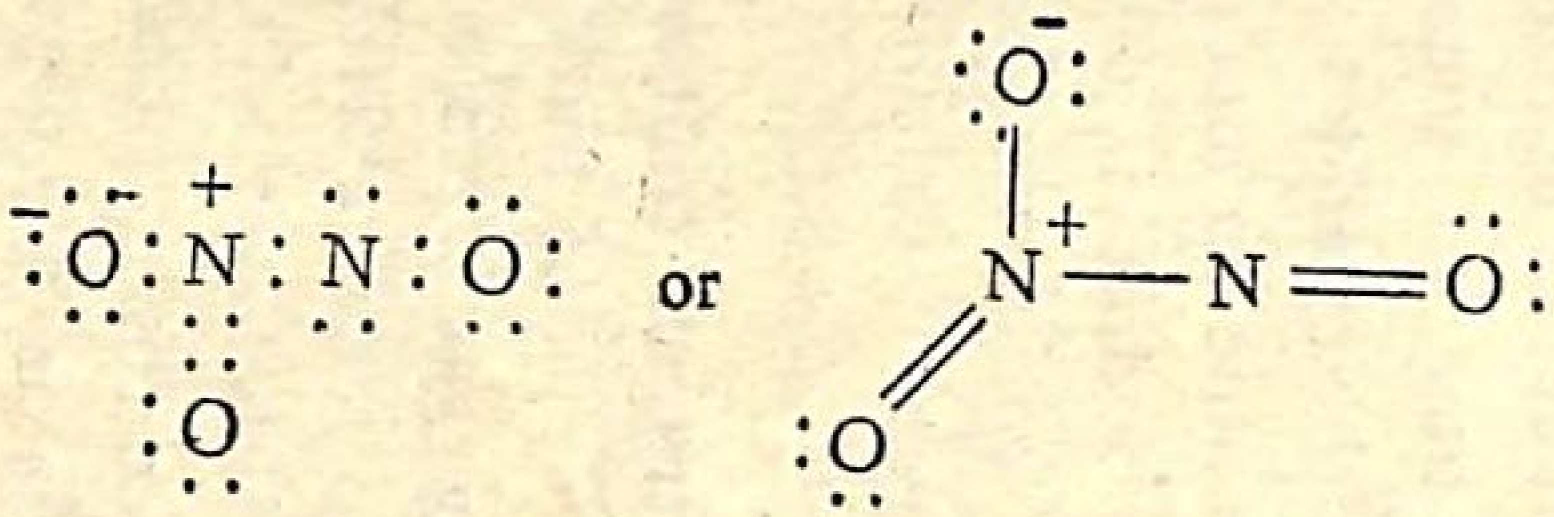


Nitrogen trichloride, NCl_3 : This is best obtained by the action of chlorine on an ammonium chloride solution below pH 4.4 :

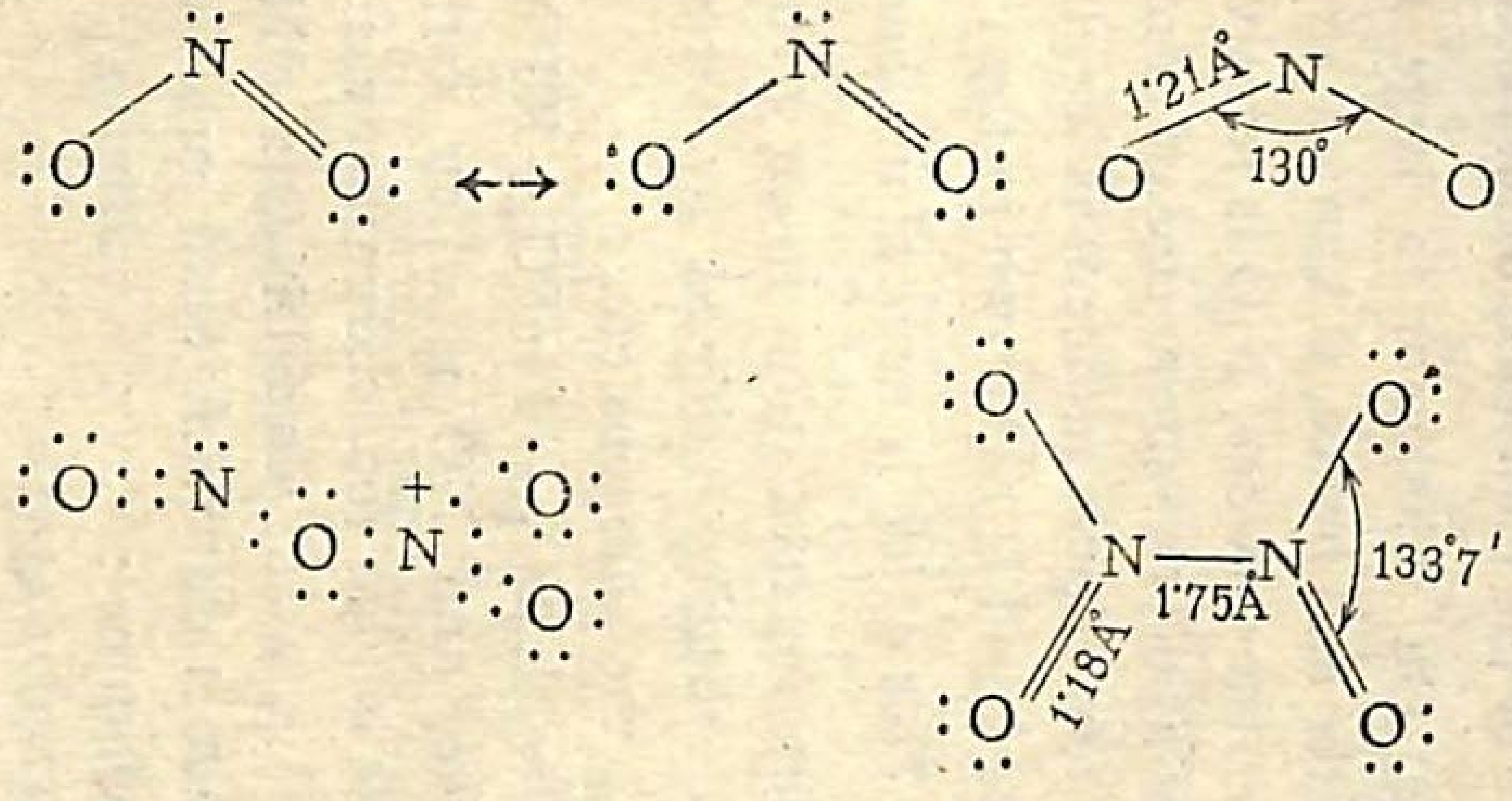
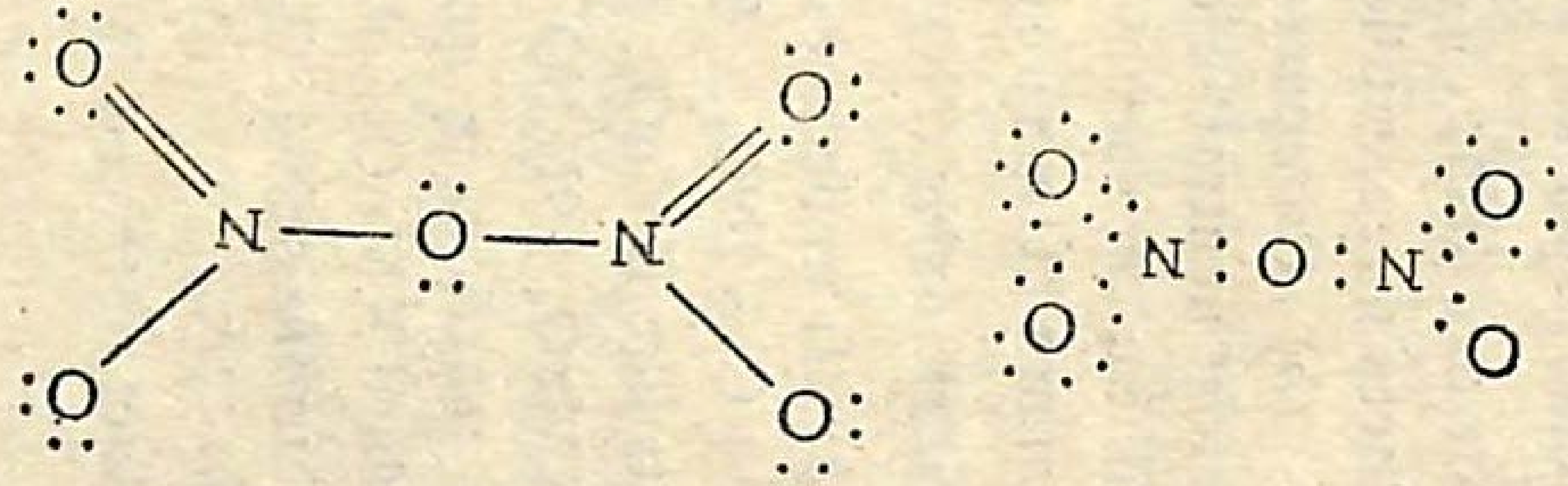
$$NH_4Cl+3Cl_2=NCl_3+4HCl.$$

It is a pale yellow liquid, boiling at 70°C. Unlike NF_3, it is vigorously hydrolysed by water for reasons discussed previously. Structurally it is similar to NF_3, but its dipole moment is larger than that of NF_3, because of the more polar character of N—Cl bond.

Oxides of nitrogen : The following table contains the formulae, names, most important methods of preparation, state of aggregation and structure of the oxides of nitrogen :

Formula & name	Method of preparation with chemical eqn.	State of aggregation and structure	
N_2O nitrous oxide (laughing gas)	By heating ammonium nitrate at ~240°C. $NH_4NO_3 \rightarrow N_2O + 2H_2O$. It is freed from contaminated NO by passing through $FeSO_4$ soln.	Colourless gas at ordinary temp.	
NO nitric oxide	(1) By the action of cold dil. HNO_3 on Cu-turnings (laboratory method) : $3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO$. (2) By catalytic oxidation of ammonia (commercial method) $4NH_3 + 5O_2 \xrightarrow[750-900°C]{\text{Pt-gauge}} 4NO + 6H_2O$	Colourless gas at ordinary temp.	
N_2O_3 dinitrogen-trioxide.	By the reduction of 50% HNO_3 with As_2O_3 (laboratory method) or metallic copper. $2HNO_3 + As_2O_3 + 2H_2O \rightarrow + N_2O_3 + H_3AsO_4$; $2Cu + 6HNO_3 \rightarrow 2Cu(NO_3)_2 + N_2O_3 + 3H_2O$.	A blue solid which decomposes above −20°C to a mixture of NO and NO_2 and hence, at room temp., N_2O_3 is an equimolecular mixture of NO and NO_2.	

Continued

Formula & name	Method of preparation with chemical eqn.	State of aggregation and structure
NO_2 & N_2O_4 nitrogen dioxide and dinitrogen tetroxide.	(1) By heating heavy metal nitrates : $2Pb(NO_3)_2 \rightarrow 2PbO + 4NO_2 + O_2$. The gas evolved is passed through U-tube put in freezing mixture, when NO_2 condenses as a brown liquid and O_2 goes out. (2) By the areal oxidation of nitric oxide $2NO + O_2 \rightarrow 2NO_2$.	NO_2 is a brown gas at ordinary temperature. In the solid state, below −11.2°C, it exists as a colourless solid of molecular formula N_2O_4. These two oxides are in a temp. dependent equilibrium $N_2O_4 \rightleftharpoons 2NO_2$. 
N_2O_5 dinitrogen pentoxide	It is obtained by the dehydration of conc. HNO_3 by P_4O_{10} in presence of ozonised oxygen. $4HNO_3 + P_4O_{10} \rightarrow 2N_2O_5 + 4HPO_3$.	Colourless crystals below 0°C. At room temp., it is yellowish coloured due to partial dissociation into NO_2 : $2N_2O_5 \rightarrow 2NO_2 + O_2$ 

Some important properties of the individual oxides of nitrogen.

Nitrous oxide (N_2O) : (*a*) On inhalation in large quantities, it produces uncontrolled laughter and hence, is known as the *laughing gas.* (*b*) Compared to the other oxides, N_2O is relatively inert. It is almost neutral in character and is a supporter of combustion. It is a linear molecule and its low dipole moment is explained by the resonance between structures I and II as shown in the table.

Nitric oxide (NO) : (*a*) This oxide is neutral in character.

(*b*) It undergoes spontaneous oxidation in air giving NO_2 : $2NO+O_2=2NO_2$. It is also readily oxidised by strong oxidising agents like $KMnO_4$, $K_2Cr_2O_7$, the halogens etc. :

$$6KMnO_4+9H_2SO_4+10NO=3K_2SO_4+6MnSO_4+10HNO_3+4H_2O.$$

This reaction is quantitative, and NO is often estimated using standard $KMnO_4$ soln. (*c*) It is also reduced rather easily : (i) when sulphurous acid (SO_2+water) is used, we get N_2O : $2NO+H_2SO_3=N_2O+H_2SO_4$; (ii) on reduction with Sn^{+2} or Cr^{+2} ions, the product obtained is hydroxylamine :

$$2NO+6H^+\xrightarrow[Cr^{+2}]{Sn^{+2}}2NH_2OH.$$

(*d*) Nitric oxide combines directly with halogens to give the corresponding nitrosyl halides (NOX) :

$$2NO + \underset{\text{halogen}}{X_2} \longrightarrow \underset{\text{nitrosyl halide}}{2NOX}$$

From the counting of the total number of electrons, the NO molecule should be an 'odd-molecule' with the alternative structures I and II (See the Table).

But, then it would have been paramagnetic and coloured, with a tendency to dimerize to pair up the odd electrons. It is much less reactive than other odd molecules. But, the structure (III) given in the table, [in which an effective three-electron bond (See p. 143-44, vol. I) is present and which may be visualised to be produced as a result of resonance between the structures I and II] can explain all the observed properties of NO. Because of its rather unusual electronic structure, the NO molecule is capable of entering into chemical combination in three different ways which will be discussed under the *nitrosyl compounds.*

Dinitrogen trioxide (N_2O_3) : This is an acidic oxide and is a mixture of NO and NO_2 at ordinary temperatures. It yields a solution of nitrous acid on dissolution in water : $N_2O_3+H_2O=2HNO_2$.

Nitrogen dioxide (NO_2) and dinitrogen tetroxide (N_2O_4) : The following temperature-dependent equilibrium exists in this case :

$$N_2O_4 \xrightleftharpoons{12^\circ-140^\circ} 2NO_2 \xrightleftharpoons{141^\circ-620^\circ} 2NO+O_2$$

NO_2 is an acidic oxide and reacts with alkalis at 300°C to produce pure nitrite (industrial preparation of KNO_2) :

$$NO+NO_2+2KOH=2KNO_2+H_2O.$$

Due to its high dielectric constant in the liquid state and its auto-ionization, $N_2O_4 \rightleftharpoons NO^+ + NO_3^-$, liquid dinitrogen tetroxide is a good solvent for acid-base reactions (see p. 219–220, vol. I).

Dinitrogen pentoxide (N_2O_5) : (*a*) This is an acidic oxide and may be regarded as the anhydride of nitric acid. It acts vigorously with water to produce nitric acid :

$$N_2O_5+H_2O=2HNO_3.$$

It acts as a strong oxidant.

Oxy-acids of nitrogen : The tables at p. 134 & 135 contain the formulae, the names, most important method of preparation, the state of aggregation and the present accepted structures of the oxy-acids of nitrogen.

Some important properties of the individual oxy-acids of nitrogen.

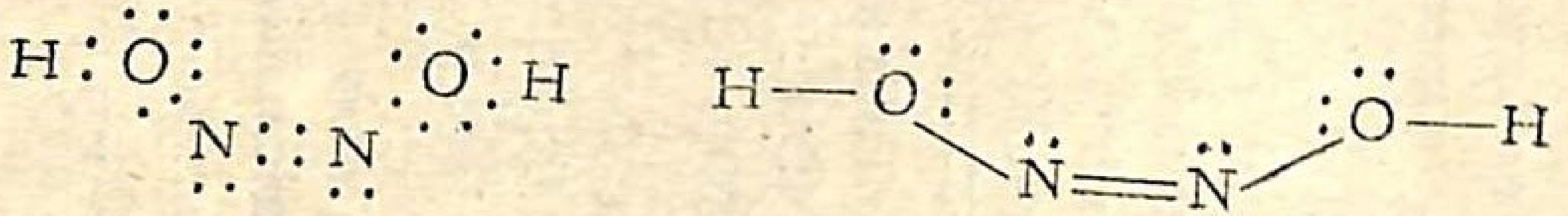
Hyponitrous acid, $H_2N_2O_2$.—It is a very weak dibasic acid, yielding both acid and normal salts, such as KHN_2O_2 and $K_2N_2O_2$.

In aqueous solution, it decomposes irreversibly :

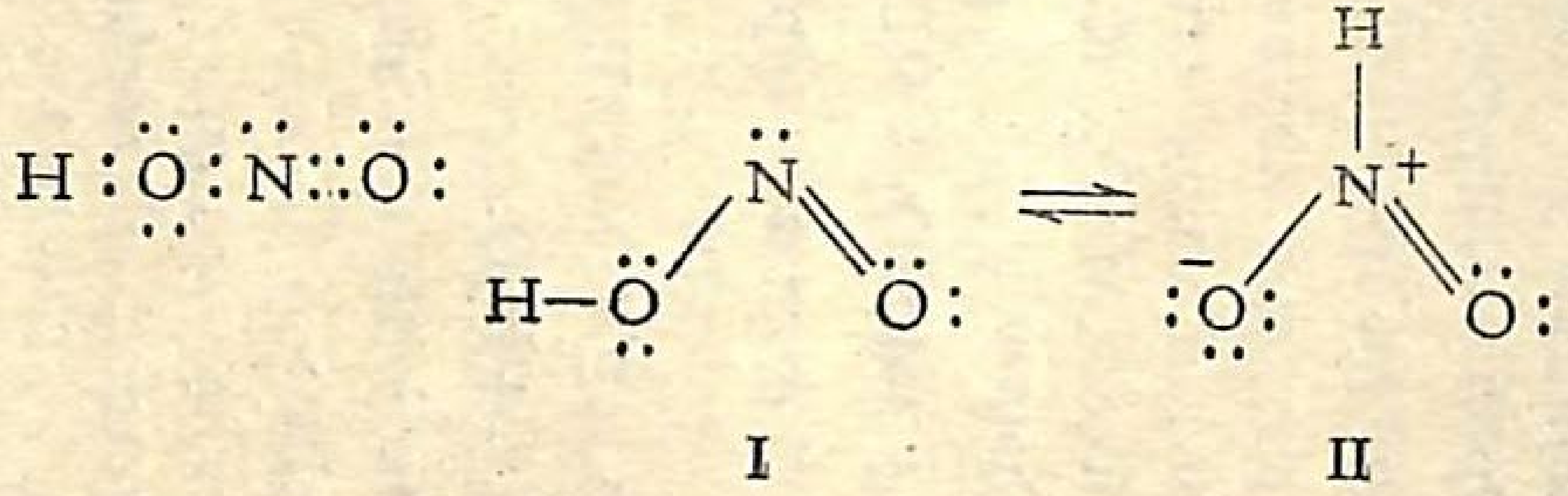
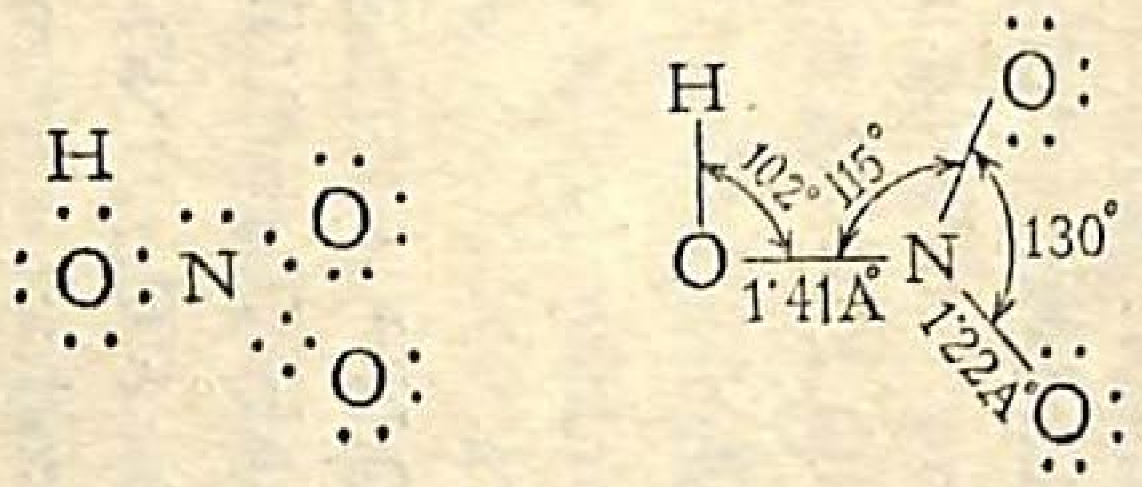
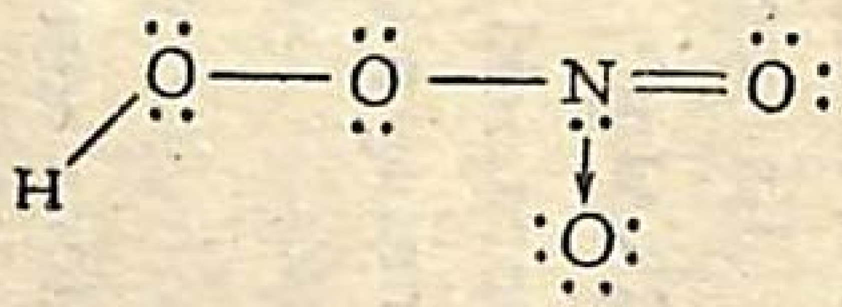
$H_2N_2O_2=N_2O+H_2O$. It behaves as a strong reducing agent.

Dipole moment (See vol. I, p. 160) of this acid molecule is found to be zero. This can be explained by its accepted structure, which is the *trans-form.*

Nitrous acid, HNO_2.—It is a weak monobasic acid which undergoes slow decomposition and spontaneously forms nitric acid and nitric oxide : $3HNO_2=HNO_3+2NO+H_2O$. This reaction may be viewed as the *auto-oxidation* or *disproportionation* of HNO_2.

Formula & name	Method of preparation.	State of aggregation and structure	
$H_2N_2O_2$ Hyponitrous acid.	The free acid is prepared by treating silver hyponitrite with an ethereal solution of HCl : $Ag_2N_2O_2 + 2HCl \rightarrow H_2N_2O_2 + AgCl\downarrow$ The ethereal solution is evaporated in vacuum to dryness.	White leaflets (hygroscopic).	
H_2NO_2 Hydronitrous acid or Nitroxylic acid.	The free acid is not isolated. The sodium salt is prepared by reacting sodium nitrite with sodium metal dissolved in liquid ammonia. $NaNO_2 + Na \rightarrow Na_2NO_2$.	Yellow powder.	Structure not known with certainty
$H_2N_2O_3$ Nitro-hydroxylamic acid or Hyponitric acid.	The sodium salt is prepared by the reaction of pure hydroxylamine in methanol with ethyl nitrate in presence of sodium ethoxide : $NH_2OH + C_2H_5NO_3 \xrightarrow{C_2H_5ONa} Na_2N_2O_3 + C_2H_5OH + H_2O$	The free acid has not been isolated. The sodium salt is stable.	Structure not known with certainty

Continued

Formula & name	Method of preparation.	State of aggregation and structure	
HNO_2 Nitrous acid.	The free acid has not been isolated. Aqueous solutions of nitrous acid is prepared by the action of calculated quantity of cold dilute mineral acid (HCl or H_2SO_4) on nitrites : $Ba(NO_2)_2 + H_2SO_4 \rightarrow BaSO_4 \downarrow + 2HNO_2$	It exists only in solution which slowly decomposes to nitric acid.	 I II
HNO_3 Nitric acid.	Conveniently prepared by heating sodium or potassium nitrate with conc. H_2SO_4. $NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3 \uparrow$. Vapours of HNO_3 condense in a receiver cooled by water.	Pure nitric acid is a colourless liquid freezing at −41.5°.	
HNO_4 Pernitric acid or peroxy nitric acid.	It is prepared by dissolving N_2O_5 in anhydrous H_2O_2. $N_2O_5 + H_2O_2 = HNO_3 + HNO_4$	It is an unstable, explosive liquid.	

It acts both as (i) an oxidising and (ii) a reducing agent.

(i) It oxidises iodide to iodine in acid solution :

$$2HNO_2+2I^-+2H^+=I_2+2NO\uparrow+4H_2O.$$

This reaction is quantitative and is used for the determination of nitrite. After treatment with excess KI, the liberated iodine is titrated with a standard thiosulphate solution, using starch indicator.

(ii) It reduces strong oxidising agents like $KMnO_4$, $K_2Cr_2O_7$, H_2O_2 etc. Its reaction with $KMnO_4$ is given below :

$$2KMnO_4+5HNO_2+3H_2SO_4=K_2SO_4+2MnSO_4+5HNO_3+3H_2O.$$

Nitrous acid rapidly decomposes urea and primary aliphatic amines, liberating nitrogen :

$$H_2N.CO.NH_2+2HNO_2=CO_2+2N_2\uparrow+3H_2O\ ;$$
$$R\text{-}NH_2+HNO_2=ROH+N_2\uparrow+H_2O.$$

At temperatures 0° – 5°C, HNO_2 reacts with the aromatic amine hydrochlorides to produce diazonium salts :

$$\underset{\text{Aniline hydrochloride}}{C_6H_5NH_2.HCl}+HNO_2 \rightarrow \underset{\text{Benzene diazonium chloride}}{C_6H_5N=N-Cl}+2H_2O.$$

Two types of organic derivatives of nitrous acid are well-known. The nitrites, R-O-NO and the nitro-compounds, $R\text{-}NO_2$. Thus, when ethyl bromide is heated with silver nitrite, both nitroethane, $C_2H_5NO_2$, and ethyl nitrite, C_2H_5ONO, are obtained.

The accepted structure of nitrous acid involves the tautomerism between the forms I and II (See table). It is quite clear that the form I yields the nitrite, while the form II is responsible for the production of the nitro-derivative.

Nitrites : These are metallic derivatives or salts of nitrous acid and, of the large number of known nitrites, sodium and potassium nitrites are of real importance.

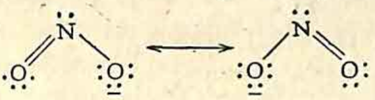
Method of preparation.—The following are the two general methods by which Na- or K-nitrites can be prepared : (i) By heating the corresponding nitrates :

$$2KNO_3\xrightarrow{\text{heat}}2KNO_2+O_2.$$

(ii) By dissolving NO and NO_2 in equimolecular proportion in caustic alkalis : $2KOH+NO+NO_2=2KNO_2+H_2O.$

The alkali metal nitrites are white crystalline solids, highly soluble in water.

The structure of the nitrite ion is best represented as a resonance hybrid of the following two structures :



Nitric acid (HNO_3) : This is the most important oxy-acid of nitrogen. It is a very strong monobasic acid which forms a constant-boiling mixture with water (b. p. 121°C) with a composition of 68·4% HNO_3. In terms of normality, this is a 16 (N) solution of HNO_3 in water, which is the concentrated nitric acid of commerce.

Nitric acid forms salts by reacting with oxides, hydroxides and carbonates of metals, and these are known as nitrates.

Apart from undergoing the usual reactions of a strong protonic acid, HNO_3 acts as an oxidising agent, dissolving some noble metals. It oxidises the non-metals to their highest oxides or oxy-acids. However, the actual products of the reactions depend on the reaction conditions.

Concentrated nitric acid (~16N) is a very strong oxidising agent. It reacts with the *active metals* (lying above hydrogen in the electrochemical series), producing ammonium ion :

$NO_3^- + 4M + 10H^+ = 4M^{+2} + NH_4^+ + 3H_2O$, where M=Mg, Zn, etc.

It is quite evident from this equation that, such oxidations by the nitrate ion will be very sensitive to the hydrogen-ion concentration of the solution in which such reactions take place. The *half-reactions* (see volume I, p 251), given below, reflect how the oxidising power of the nitrate ion and its reduction products depend on the acid concentration :

(a) $NO_3^- + 10H^+ + 8e \rightarrow NH_4^+ + 3H_2O$; $E° = 0{\cdot}88V$

(b) $NO_3^- + 7H^+ + 6e \rightarrow NH_2OH + 2H_2O$; $E° = 0.96V$

(c) $NO_3^- + 6H^+ + 5e \rightarrow \frac{1}{2}N_2 + 3H_2O$; $E° = 1{\cdot}25V$

(d) $NO_3^- + 4H^+ + 3e \rightarrow NO + 2H_2O$; $E° = 0{\cdot}96V$

(e) $NO_3^- + 2H^+ + e \rightarrow NO_2 + H_2O$; $E° = 0{\cdot}80V$

The reactions (d) and (e) take place with weak reducing agents like the noble metals—copper and silver. The reactions (a) to (c) take place with stronger reducing agents like the active metals, Zn, Mg, Fe, Sn etc. In fact, below a concentration of 2N, the oxidising power of the nitrate ion is so much reduced that only the protons generated by the dissociation of nitric acid react with the active metals, liberating hydrogen :

$$\begin{array}{c} 2HNO_3 = 2H^+ + 2NO_3^- \\ M + 2H^+ = M^{++} + H_2\uparrow \\ \hline M + 2HNO_3 = M^{++} + 2NO_3^- + H_2\uparrow \end{array} \quad (M = Zn,\ Mg,\ Fe)$$

The concentrated acid reacts even with the *noble metals* or *inactive metals* (lying below hydrogen in the electrochemical series), producing nitric oxide :

$$3Cu + 2NO_3^- + 8H^+ \rightarrow 3Cu^{+2} + 2NO + 4H_2O.$$

Some typical oxidation reactions of nitric acid are given below :

With cold, dilute HNO_3 of strength $\sim 5N$:

$$\begin{array}{c} 4M + 8HNO_3 \rightarrow 4M(NO_3)_2 + 8\,H] \\ 2HNO_3 + 8[H] \rightarrow N_2O + 5H_2O \\ \hline 4M + 10HNO_3 = 4M(NO_3)_2 + N_2O + 5H_2O. \end{array}$$

With a more dilute acid ($\sim 3-2N$) in the cold, the following reaction takes place :

$$\begin{array}{c} 5M + 10HNO_3 \rightarrow 5M(NO_3)_2 + 10[H] \\ 2HNO_3 + 10[H] \rightarrow N_2 + 6H_2O \\ \hline 5M + 12HNO_3 = 5M(NO_3)_2 + N_2 + 6H_2O \end{array}$$

$(M = Zn,\ Mg,\ Fe).$

Reactions with some non-metals : As already mentioned, the non-metals are oxidised by conc. HNO_3 to their highest oxy-acids (or oxides, when the oxy-acid is unstable) :

$$\begin{aligned} P_4 + 20HNO_3 &= 4H_3PO_4 + 20NO_2 + 4H_2O\ ; \\ C + 4HNO_3 &= CO_2 + 4NO_2 + 2H_2O\ ; \\ I_2 + 10HNO_3 &= 2HIO_3 + 10NO_2 + 4H_2O\ ; \\ S + 2HNO_3 &= H_2SO_4 + 2NO. \end{aligned}$$

Dilute nitric acid ($5-3N$) also acts as an oxidising agent towards ferrous iron, sulphides etc., itself being reduced to NO :

$$\begin{array}{c} NO^-_3 + 4H^+ + 3e \rightarrow NO + 2H_2O \\ 3Fe^{+2} \quad \rightarrow 3Fe^{+3} + 3e \\ \hline NO_3^- + 3Fe^{+2} + 4H^+ = 3Fe^{+3} + NO + 2H_2O \end{array}$$

$$\begin{array}{l} 2NO_3^- + 8H^+ + 6e \rightarrow 2NO + 4H_2O \\ 3S^{2-} \qquad\qquad \rightarrow 3S + 6e \\ \hline 2NO_3^- + 3S^{2-} + 8H^+ = 2NO + 3S\downarrow + 4H_2O \end{array}$$

The nitronium cation, NO_2^+, and nitration of organic compounds. It has been found that in a mixture of concentrated nitric and sulphuric acids, the nitronium cation, NO_2^+, is generated :

$$HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2HSO_4^-$$

This nitronium cation, NO_2^+, is the active nitrating agent which nitrates aromatic compounds when they are treated with a conc. H_2SO_4-HNO_3 mixture.

$$C_6H_6 \xrightarrow{HNO_3/H_2SO_4} C_6H_5NO_2 + H_2O.$$

Nitration of benzene is an electrophilic substitution, and NO_2^+ being a strong electrophilic reagent, performs it efficiently.

Nitrates : These are salts of nitric acid and can be conveniently prepared by (i) the action of nitric acid on a metal, or (ii) by dissolving a metal carbonate or oxide in nitric acid.

All nitrates, excepting the sub-nitrates (e.g. bismuth sub-nitrate, $BiONO_3$) are crystalline solids, highly soluble in water. On heating, the alkali metal nitrates are converted into nitrites and liberate oxygen, which exerts strong oxidising action :

$$2NaNO_3 \xrightarrow{heat} 2NaNO_2 + O_2.$$

This is the reason of KNO_3 or $NaNO_3$ being used as the oxidising agent along with sodium carbonate in the *fusion test* for detecting chromium and manganese in inorganic salt-mixtures. If the mixture contains a manganese salt, it turns green on fusion with Na_2CO_3 and $NaNO_3$:

$$\begin{array}{c} 2NaNO_3 \rightarrow 2NaNO_2 + O_2 \\ MnO + O_2 + Na_2CO_3 \rightarrow Na_2MnO_4 + CO_2\uparrow \\ \hline MnO + 2NaNO_3 + Na_2CO_3 = \underset{\text{sodium manganate (green).}}{Na_2MnO_4} + 2NaNO_2 + CO_2\uparrow \end{array}$$

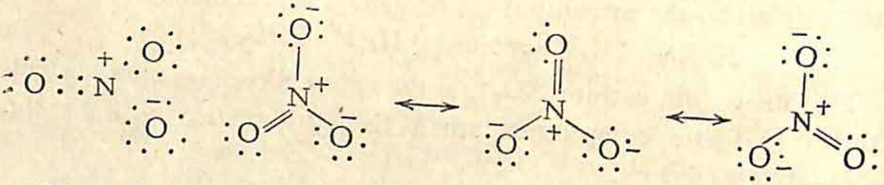
In a similar manner, if the colour of the mixture turns yellow on fusion with $NaNO_3$ and Na_2CO_3, the presence of chromium is indicated.

$$6NaNO_3 \rightarrow 6NaNO_2 + 3O_2$$

$$2Cr_2O_3 + 3O_2 + 4Na_2CO_3 \rightarrow 4Na_2CrO_4 + 4CO_2 \uparrow$$

Adding, $$2Cr_2O_3 + 6NaNO_3 + 4Na_2CO_3 = \underset{\text{yellow}}{4Na_2CrO_4} + 6NaNO_2 + 4CO_2 \uparrow .$$

The overall structure of the nitrate ion is conveniently represented as a hybrid of the following resonating structures :



Manufacture of nitric acid.

From ammonia ; At present, nitric acid is manufactured mostly by the catalytic oxidation of ammonia (obtained by the Haber process) by **Ostwald's process.**

Materials : Ammonia is obtained by the Haber process. Air is freed from dust and dried by passing through drying columns. The catalyst used is platinum or Pt-Rh gauge.

Method : Ammonia is mixed with 10 vols. of air and rapidly passed over platinum or platinum-rhodium gauge kept at 750-900°C, when it is oxidised to nitric oxide :

$$4NH_3 + 5O_2 \xrightarrow[\sim 800^\circ C]{\text{Pt-gauge}} 4NO + 6H_2O \; ; \; (\Delta H = -21 \cdot 5 \text{ Kcals.})$$

Once the reaction is started, no further external heating of the catalyst is necessary. The heat evolved in this exothermic reaction maintains the required temperature.

The nitric oxide produced is then oxidised by the aerial oxygen, still left, to NO_2 which is absorbed in water in presence of air to yield nitric acid :

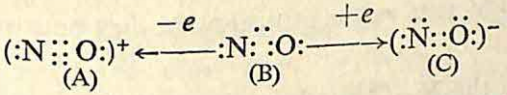
$$2NO + O_2 \rightarrow 2NO_2 \; ;$$

$$4NO_2 + 2H_2O + O_2 \rightarrow 4HNO_3 .$$

Pure nitric acid can be obtained by distilling any dilute acid with sufficient conc. H_2SO_4. Fuming nitric acid is produced by dissolving NO_2 in concentrated nitric acid till it is saturated. It is brown coloured due to the presence of dissolved NO_2 in it.

Uses of nitric acid : The largest use of nitric acid (as the mixed acid) is as a nitrating agent for organic compounds, especially in the manufacture of explosives (picric acid, nitroglycerine, T. N. T. etc.), dyestuff and pharmaceuticals. Soluble nitrates like NH_4NO_3, calcium-ammonium nitrate etc. are good nitrogenous fertilizers. HNO_3 is widely used in the laboratory for dissolution of copper-base alloys and as an oxidising agent.

Nitrosyl compounds : Compounds containing the NO group, which may be obtained by the direct involvement of nitric oxide or otherwise, are called nitrosyl compounds. The electronic structure of the NO molecule creates the possibility of its participation as the neutral NO molecule, NO^+ cation and the NO^- anion, which may be represented electronically as :



$$\underset{(A)}{(:N\vdots\vdots O:)^+} \xleftarrow{-e} \underset{(B)}{:N\overset{..}{:}\,:O:} \xrightarrow{+e} \underset{(C)}{(:\dot{N}::\ddot{O}:)^-}$$

From the above electronic structures, it is quite evident that, apart from acting as a cation and an anion, all the three forms (A), (B) and (C) can act as monodentate donors, donating either the lone-pair on nitrogen or that on oxygen and hence, are capable of forming co-ordination complexes. It is to be noted also that the NO^+ species is isoelectronic with the carbon monoxide molecule. This is the reason of NO being able to substitute carbon monoxide from *metal carbonyls* and *vice-versa.* It is also isoelectronic with the nitrogen molecule and the cyanide ion.

Chemistry of the nitrosyl compounds can be conveniently discussed in brief under the following heads :

1. Simple ionic compounds containing the NO^+ cation :

Familiar examples of this class of compounds are nitrosyl bisulphate ($NOHSO_4$), nitrosyl perchlorate ($NOClO_4$) and nitrosyl fluoborate ($NOBF_4$). All of these may be obtained by the reaction of the corresponding acids (concentrated) with N_2O_3, when the NO^+ cation is generated *in situ* :

$$N_2O_3+2H_2SO_4=2NOHSO_4+H_2O\ ;$$
$$N_2O_3+2HClO_4=2NOClO_4+H_2O.$$

The ionic nature of all these compounds was evident from the conducting property of their solutions in several polar non-aqueous solvents. The presence of the NO^+ cation is established by the electrolysis of such solutions, when NO is liberated at the cathode and forms brown vapour of NO_2 on oxidation by the atmospheric oxygen.

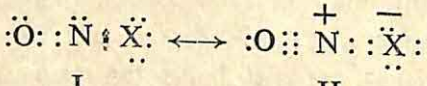
2. **Simple covalent (but polar) compounds, containing the NO^+ cation :**

The nitric oxide molecule reacts with highly electronegative halogens, forming nitrosyl halides, through the participation of its odd-electron in forming a covalent linkage :

$$2NO + X_2 \rightarrow 2NOX \text{ (where } X = F, Cl, Br).$$

The predominantly covalent nature of these compounds is indicated by their non-conducting nature and volatile character. But, their dipole moment values indicate that they possess perceptible polar character.

The lengths of the N—O bonds in nitrosyl halides are intermediate between that of a double and a triple bond and it is explained on the basis of the following resonating structures :



$$:\ddot{O}::\ddot{N}\vdots\underset{\cdot\cdot}{\ddot{X}}: \longleftrightarrow :O::\overset{+}{N}::\underset{\cdot\cdot}{\overset{-}{\ddot{X}}}:$$

I II

All the simple nitrosyl compounds containing the NO^+ cation are easily hydrolysed by water and hence, they must be prepared and kept under dry conditions.

3. **Simple ionic compounds containing the NO^- group :** The only example of this class of nitrosyl compound is NaNO, which is an unstable solid obtained by the reaction of dry nitric oxide with sodium metal dissolved in liquid ammonia. That it is quite different from sodium hyponitrite ($Na_2N_2O_2$), having the same stoichiometry, has been proved from its X-ray diffraction pattern. It also differs from sodium hyponitrite in its chemical properties. The diamagnetic character of this compound suggests the presence of the NO^- group in it.

4. **Coordination compounds containing any one of the species (A), (B) and (C).**

In these compounds, the nitrosyl entity is directly associated with metal ions or atoms. It has been found that co-ordination to the metal ion or atom is always through the lone-pair located on the nitrogen. Thus, when the nitroprusside ion $[Fe(CN)_5NO]^{2-}$ is reduced, the product is the ammine, $[Fe(CN)_5(NH_3)]^{3-}$. The same nitroprusside ion is converted to the nitro-derivative, $[Fe(CN)_5(NO_2)]^{4-}$ by an alkali. In both the cases, the nitrogen of the nitrosyl entity is retained.

Depending on the presence of the forms (A) (B) and (C) in them, the nitrosyl complexes may be divided into three different categories :

(i) **Nitrosyl complexes containing coordinated neutral NO molecule (B)** : The present experimental evidence precludes the co-ordination of the neutral NO group to a metal atom or ion, and no well-established example of this class is known.

(ii) **Nitrosyl complexes containing the NO^- entity (A)** : An established example of this class is $[Co(NH_3)_5NO]^{+2}$, where cobalt (II) appears to transfer one electron to the NO group. The diamagnetic character of this compound supports this. A few other examples of such compounds are $[Ru(NH_3)_4(H_2O)(NO)]^{+3}$ and $[Ru(NH_3)_4(Cl)(NO)]^{+2}$. These two compounds are also diamagnetic.

(iii) **Nitrosyl complexes containing the NO^+ entity (C)** : Since the NO^+ entity is *isosteric* with carbon monoxide, cyanide ion and the nitrogen molecule, it has the potentials of an efficient donor like the CO or CN^- species. Most of the known nitrosyl complexes thus contain the NO^+ entity. It is to be appreciated that in the formation of the NO^+ cation, the electron lost by the nitric oxide molecule may be transferred to the metal ion or atom, acting as the acceptor, thus decreasing the positive oxidation state of the acceptor by one unit. This view has been substantiated by the overall oxidation state of the compounds like sodium nitroprusside, $[Fe(CN)_5NO]^{2-}$, which is obtained by the nitrosoation of the ferricyanide ion, $[Fe^{III}(CN)_6]^{3-}$. Transfer of one electron from the NO group to the Fe^{+3} of the ferricyanide converts it into Fe^{+2} and results in the formation of the NO^+ cation. Thus, in the co-ordination zone of the nitroprusside ion, five negative charges due to five CN^- ions and three positive charges consisting of one Fe^{+2} and one NO^+, make the overall charge on the nitroprusside ion equal to -2.

Some examples of this class of nitrosyl complexes are : (a) nitrosyl carbonyls such as $Co(NO)(CO)_3$, $Fe(NO)_2(CO)_2$; (b) metal nitrosyl hydroxides and halides, such as $Ni(NO)(OR)(OH)$, $Fe_2(NO)_4I_3$ and $Co(NO)_3X(X=Cl, Br, I)$; (c) metal nitrosyl thio-compounds like $M^I[Fe(NO)_2S]$ (where $M=Na^+$, K^+, NH_4^+), which are known as the Roussins salts; (d) nitrosyl complexes of the type $M^{II}(NO)_xA_y$, such as $Fe(NO)SeO_4.H_2O$, $Fe(NO)(R_2NCS_2)_2$; (e) nitrosyl complexes of the type $M^{III}(NO)_xA_y$, such as $Fe_2(NO)_2(SO_4)_3$ and $Ru(NO)(R_2NCS_2)_3$; (f) nitrosyl complexes of the type $[MA_5(NO)]^{+n}$, such as $[Mn(CN)_5(NO)]^{3-}$, $[Fe(CN)_5(NO)]^{2-}$ and $[Ni(NH_3)_5(NO)]^+$; (g) miscellaneous nitrosyl complexes such as Roussins black salts, $M^I[Fe_4(NO)_7S_3](M=Na^+$, K^+, Rb^+ etc.).

PHOSPHORUS

Due to its high reactivity, phosphorus is never found in nature in the free state. It is generally found in nature in its highest oxidation state as the various phosphates. Some important phosphorus-bearing minerals are :

Fluorapatite, $3Ca_3(PO_4)_2, CaF_2$;
Phosphorite, $Ca_3(PO_4)_2$;
Chlorapatite, $3Ca_3(PO_4)_2, CaCl_2$.

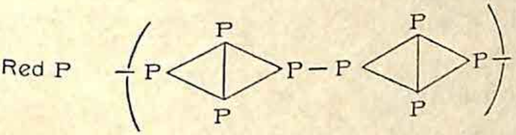
Bones of human beings and other animals contain high percentages of $Ca_3(PO_4)_2$.

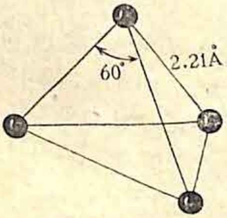
Industrially, phosphorus is manufactured by heating any one of the above minerals (finely powdered) with sand and coke in an electric furnace at 1200° – 1500°C. In the first phase, calcium phosphate reacts with silica by the process of double decomposition and produces calcium silicate and phosphorus pentoxide: $Ca_3(PO_4)_2+3SiO_2=3CaSiO_3+P_2O_5$. In the second step, this P_2O_5 is reduced by coke to elemental phosphorus : $P_2O_5+5C=2P+5CO$.

At the temperature of the furnace (1200° – 1500°C), phosphorus is vaporised and passes out through the outlet at the top, along with CO, and is passed into a reservoir containing cold water and is condensed. The water layer above the elemental phosphorus also protects it from being oxidised by atmospheric air.

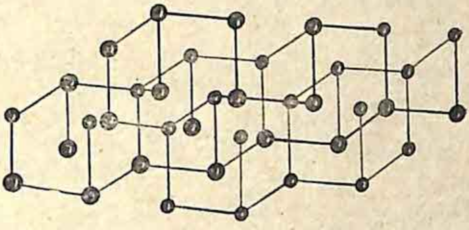
Purification : The crude phosphorus is first melted under a mixture of $K_2Cr_2O_7$ and H_2SO_4, when oxidisable impurities are removed. It is then distilled in absence of air, when very pure (white) phosphorus is obtained.

Allotropic modifications of phosphorus : As already discussed at the beginning of this chapter, phosphorus exists mainly in three allotropic modifications, *viz*. *white*, *red* and *black* phosphorus. The difference in the properties of these three forms are due to the difference in their structures. White phosphorus is made up of tetrahedrally arranged P_4 units, the P—P—P bond angle is 60° and hence, the P_4 molecule is under considerable strain. Black phosphorus is made up of almost strainless hexagonal rings with P—P—P bond angles of 100° and cross-linkings among the different rings. Red phosphorus occurs with tetrahedrally arranged P_4 units joined in a chain.

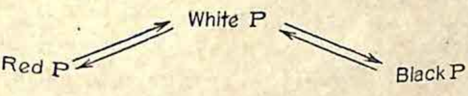




White P



Black P



The structure of white phosphorus explains its volatility (Mol. Wt. of P_4 molecule=124) compared to the red and the black forms, and its high reactivity is due to the considerable strain existing in the P_4 molecule with P—P—P angles of 60°. The very low reactivity of the black phosphorus is due to its polymeric structure with P—P—P angles of 100°, which involves very little strain. The red phosphorus obviously possesses an intermediate reactivity.

Uses of phosphorus : Phosphorus (mainly the red variety) is used in the manufacture of matches, tracer bullets, incendiary bombs etc. It is used in the manufacture of alloys like phosphor bronze.

It is also used for the manufacture of insecticides and herbicides.

Phosphorus is widely used in the preparation of phosphoric acid, hypophosphites etc., which find large use in medicine and fertilizer industries.

Phosphides : The phosphides are obtained by the direct combination of phosphorus with metals. Gr IA and IIA metals combine directly with phosphorus, producing phosphides like Na_3P, Ca_3P_2, Mg_3P_2 etc. These compounds possess some ionic character and react with water to produce phosphine : $Ca_3P_2+6H_2O=3Ca(OH)_2+2PH_3$.

The Gr IIIA elements, Al and B, form phosphides like AlP and BP which exhibit some covalent character.

Several transition elements form compounds with phosphorus, having the compositions FeP, Fe_2P, OsP_2, RuP etc. These are dark solids with metallic lustre and conduct electricity. They do not react with water and may be regarded as *interstitial compounds*.

Hydrides : Phosphorus is said to form a series of hydrides such as PH_3, P_2H_4, $P_{12}H_6$, P_5H_2 etc. Of these, the first two are fully characterised and may be considered as the analogues of NH_3 and N_2H_4.

Phosphine, PH_3 : It may be prepared by any one of the following methods :

(1) By heating white phosphorus with concentrated aqueous sodium hydroxide solution in an inert atmosphere of CO_2 or coal gas :

$$P_4+3NaOH+3H_2O=\underset{\text{sodium hypophosphite}}{3NaH_2PO_2}+PH_3\uparrow$$

(ii) It can be obtained conveniently by hydrolysing calcium or aluminium phosphide with dilute mineral acids :

$$Ca_3P_2+6H_2O\xrightarrow{\text{acid}}2PH_3+3Ca(OH)_2$$

Some diphosphine is also produced, which condenses as a yellow liquid when cooled in a freezing mixture, while PH_3 passes out as a gas.

Phosphine is a colourless, inflammable gas, with a smell of rotten fish. It is slightly soluble in water and the solution is not alkaline. Most of its properties have been discussed in the comparative evaluation of the hydrides of the Gr.VB elements in general. It precipitates the phosphides of copper and silver from their salts :

$$3CuSO_4 + 2PH_3 = Cu_3P_2 \downarrow + 3H_2SO_4 \ ;$$
$$3AgNO_3 + PH_3 = Ag_3P \downarrow + 3HNO_3 \ .$$

Due to the less electronegative character (compared to nitrogen) of phosphorus, PH_3 does not form complexes as ammonia does. But, the alkyl and aryl phosphines are fairly good donors.

Diphosphine, P_2H_4 : Diphosphine is obtained as a by-product of the preparation of PH_3 from Ca_3P_2.

It is a spontaneously inflammable gas which decomposes at room temperature to an amorphous yellowish solid of undefined composition, consisting of phosphorus and hydrogen.

Though P_2H_4 is analogous to N_2H_4 in composition, it has no basic character like N_2H_4, which again can be attributed to the much less electronegative character of phosphorus in comparison to that of nitrogen.

The structures of PH_3 and P_2H_4 are similar to those of NH_3 and N_2H_4 respectively.

Oxides of phosphorus : The following table contains the formulae, names, the most important method of preparation and the state of aggregation of the oxides of phosphorus :

Formula and name	Method of preparation	State of aggregation
P_4O_6 Phosphorus trioxide	It is prepared by burning white phosphorus in a limited supply of air. It contains P_4O_{10} which is freed by condensing the P_4O_{10} vapour to solid at 60°, when the P_4O_6 vapour passes out and is collected in a receiver at room temp. $P_4 + 3O_2 \rightarrow P_4O_6$	White waxy solid with garlic-like odour. Highly poisonous.
P_4O_{10} Phosphorus pentoxide	Prepared by burning white phosphorus in excess of air. $P_4 + 5O_2 \rightarrow P_4O_{10}$	White powder, extremely hygroscopic, and exists in three crystalline modifications.

Some important properties of the individual oxides of phosphorus.

Phosphorus trioxide : It is an acidic oxide and reacts with cold water to produce phosphorous acid :

$$P_4O_6+6H_2O=4H_3PO_3.$$

On reaction with hot water, it produces phosphine and phosphoric acid :

$$P_4O_6+6H_2O\xrightarrow{\text{heat}}PH_3+3H_3PO_4.$$

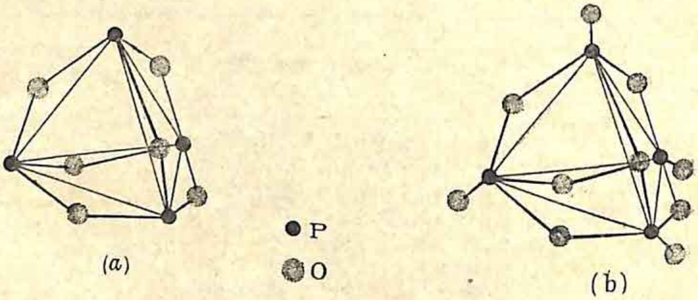
This is a case of *disproportionation* of P^{+3} to P^{-3} and P^{+5}.

It undergoes spontaneous reaction with chlorine, forming $POCl_3$ and PO_2Cl :

$$P_4O_6+4Cl_2=2POCl_3+2PO_2Cl.$$

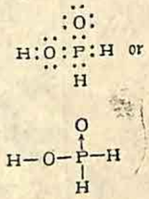
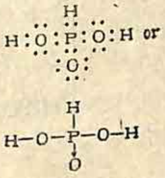
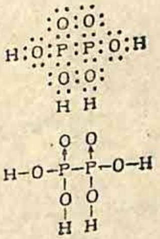
Phosphorus pentoxide : It is an acidic oxide, and depending on the amount of water added, it forms different phosphoric acids :

$$nP_4O_{10}+2nH_2O \longrightarrow 4(HPO_3)_n \quad (P_4O_{10} : H_2O=1 : 2)$$
$$P_4O_{10}+4H_2O \longrightarrow 2H_4P_2O_7 \quad (P_4O_{10} : H_2O=1 : 4)$$
$$P_4O_{10}+6H_2O \longrightarrow 4H_3PO_4 \quad (P_4O_{10} : H_2O=1 : 6)$$



Structures of P_4O_6 and P_4O_{10} are based on the structure of white phosphorus—the P_4-tetrahedra. Bridging of each of the P—P bonds of the P_4-molecule with an oxygen atom will give rise to the P_4O_6 molecule (*a*). Further addition of a doubly bonded oxygen to each of the phosphorus atoms in P_4O_6 leads to the formation of P_4O_{10} (*b*). Molecular weight determinations confirm these formulas.

Oxy-acids of phosphorus : The following table contains the formulae, the names, most important method of preparation, the state of aggregation and the present accepted structure of the oxy-acids of phosphorus.

Formula and name	Method of preparation	State of aggregation	Structure
H_3PO_2 Hypophosphorous acid.	This is prepared as its barium salt by boiling white phosphorus with barium hydroxide : $3Ba(OH)_2+8P+6H_2O =3Ba(H_2PO_2)_2+2PH_3$. The free acid is generated by the addition of calculated amount of dilute H_2SO_4 to the barium salt : $Ba(H_2PO_2)_2+H_2SO_4 =BaSO_4+2H_3PO_2$.	It is a colourless crystalline solid, melting at 26.5°C. It is a monobasic acid, readily soluble in water.	
H_3PO_3 Phosphorous acid or orthophosphorous acid.*	This acid is prepared by hydrolysing PCl_3 with water : $PCl_3+3H_2O=H_3PO_3+3HCl$.	It is a colourless crystalline solid, melting at 73°C. It is highly soluble in water and behaves as a dibasic acid.	
$H_4P_2O_6$ Hypophosphoric acid.	It may be prepared by the oxidation of red phosphorus with sodium chlorite ($NaClO_2$) in an alkaline medium. It is stable as the Na^+, K^+ or Ca^{++} salts. The free acid undergoes slow hydrolysis into orthophosphorous and orthophosphoric acids : $H_4P_2O_6+H_2O=H_3PO_3 +H_3PO_4$.	It is a white solid, melting at 95°C. It is also obtained as a crystalline dihydrate, melting at 70°C. It behaves as a tetrabasic acid and exists in solution as a dimer.	

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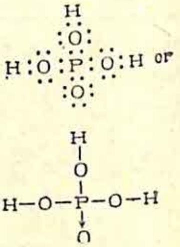
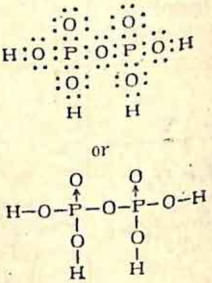
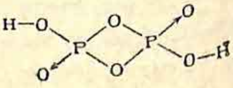
* Though metaphosphorous acid (HPO_2) and pyrophosphorous acid ($H_4P_2O_5$) are obtained as such or as salts, they are not stable, and undergo rapid hydration to the corresponding orthophosphorous varieties and hence, only the ortho variety is of real importance.

Formula and name	Method of preparation	State of aggregation	Structure
H_3PO_4 Orthophosphoric acid.	Is is conveniently prepared by oxidising white phosphorus with 1 : 1 nitric acid : $P_4+20HNO_3=4H_3PO_4+20NO_3+4H_2O$. It is also prepared by reacting P_4O_{10} with excess water in boiling condition : $P_4O_{10}+6H_2O=4H_3PO_4$. Industrially, it is obtained by reacting mineral calcium phosphate with sulphuric acid. All other phosphoric acids are ultimately hydrolysed to H_3PO_4.	Anhydrous H_3PO_4 is a solid, melting at 42.3°C. The syrupy phosphoric acid of commerce is 85% H_3PO_4. It is a tribasic acid, yielding three series of salts. Its tribasic nature is evident from the presence of three OH groups linked to the central phosphorus atom.	
$H_4P_2O_7$ Pyrophosphoric acid.	It is prepared by heating H_3PO_4 to 250–260°C : $2H_3PO_4 \rightarrow H_4P_2O_7+H_2O$. It is reconverted into H_3PO_4 by boiling with water.	It is a colourless crystalline solid which melts at 61°C. It is a tetrabasic acid which yields metaphosphoric acid, $(HPO_3)_n$, on strong heating : $H_4P_2O_7 \xrightarrow{600^\circ} 2HPO_3+H_2O$. Tetrabasic nature is evident from the presence of four OH groups in its structural formula.	
HPO_3. Metaphosphoric acid.	It is conveniently prepared by heating H_3PO_4 (or $H_4P_2O_7$) above 300°C : $H_3PO_4 \xrightarrow{\text{heat}} HPO_3+H_2O$. It can also be prepared by reacting P_4O_{10} with a small amount of water : $P_4O_{10}+2H_2O=4HPO_3$.	It is a glassy solid, melting above 38·4°C and probably exists in a polymeric state. It is a monobasic acid, soluble in water.	The simplest form of metaphosphoric acid is a dimer. 

Some important properties of the individual oxy-acids of phosphorus.

Hypophosphorous acid, H_3PO_2 : Hypophosphorous acid as well as its salts (hypophosphites) are strong redcuing agents, as they contain phosphorus in the +1 oxidation state and have a strong tendency to go to the +5 oxidation state as H_3PO_4. They reduce Cu^{+2} to cuprous hydride :

$$4Cu^{+2}+3H_3PO_2+6H_2O \rightarrow 2Cu_2H_2+3H_3PO_4+8H^+.$$

It reduces mercuric chloride first to mercurous chloride and ultimately to metallic mercury :

$$4HgCl_2+H_3PO_2+2H_2O=2Hg_2Cl_2\downarrow+H_3PO_4+4HCl\ ;$$
$$2Hg_2Cl_2+H_3PO_2+2H_2O=4Hg\downarrow+H_3PO_4+4HCl.$$

The reducing character of this acid is indicated by the presence of two P—H bonds in its molecular structure.

Phosphorous acid, H_3PO_3 : It is a dibasic acid and contains phosphorous in the +3 oxidation state and hence, the acid and its salts behave as fairly strong reducing agents (weaker than hypophosphorous acid). This is also indicated by the presence of one P—H bond in its molecular structure. Thus, it reduces Cu^{+2} and Ag^+ compounds to the respective metallic states, itself being oxidised to the +5 state in the form of H_3PO_4 :

$$H_3PO_3+Cu^{+2}+H_2O \rightarrow Cu\downarrow+H_3PO_4+2H^+\ ;$$
$$H_3PO_3+2Ag^++H_2O \rightarrow 2Ag\downarrow+H_3PO_4+2H^+.$$

On heating, H_3PO_3 decomposes to PH_3 and H_3PO_4 :

$$4H_3PO_3=3H_3PO_4+PH_3.$$

Phosphoric acid, H_3PO_4 : It is a fairly strong tribasic acid and is capable of ionization in three stages :

$$H_3PO_4 \rightleftharpoons H^+ + \underset{\text{dihydrogen phosphate ion}}{H_2PO_4^-} \qquad K_1=7.2\times10^{-3}$$

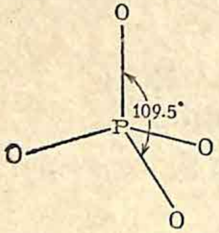
$$H_2PO_4^- \rightleftharpoons H^+ + \underset{\text{monohydrogen phosphate ion}}{HPO_4^{2-}} \qquad K_2=6{\cdot}2\times10^{-8}$$

$$HPO_4^{2-} \rightleftharpoons H^+ + \underset{\text{phosphate ion}}{PO_4^{3-}} \qquad K_3=1\times10^{-13}$$

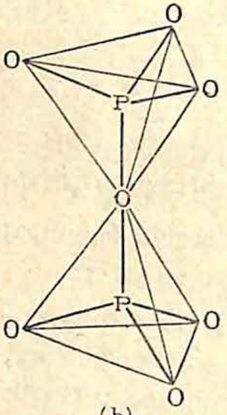
It is clear from the values of the successive ionization constants given above that, in a dilute aqueous solution, the first ionization takes place easily and the second ionization takes place to a slight extent, while the third-step ionization is negligible. However, it forms three series of salts. The structures of the orthophosphate ion (*a*) and the pyrophosphate ion (*b*) are given below :

It is evident from these figures that the PO_4^{3-} ion is tetrahedral, with the phosphorus atom near the centre of the tetrahedron. The structure of the $P_2O_7^{4-}$ ion is derived from the PO_4^{3-} tetrahedron, with one corner shared between the two tetrahedra.

Phosphoric acid finds wide use in industry in the manufacture of ammonium, alkali and alkaline earth phosphate-fertilizers and the corresponding glycero-phosphates. Mono- and di-sodium/potassium salts are widely used as *buffers*.



(*a*)



(b)

Metaphosphoric acid and metaphosphates : Metaphosphoric acid is never obtained as the monomer, HPO_3. It is best represented as $(HPO_3)_n$, where *n* generally has an integral value between 2 and 6. The simplest form is the dimer $(HPO_3)_2$. It is a fairly strong dibasic acid with $K_1=1.6\times10^{-2}$ and $K_2=7\times10^{-7}$. High polymers of metaphosphates with cyclic structure are also known.

The alkali metal metaphosphates are generally obtained by heating NaH_2PO_4, KH_2PO_4 or $Na_2H_2P_2O_7$.

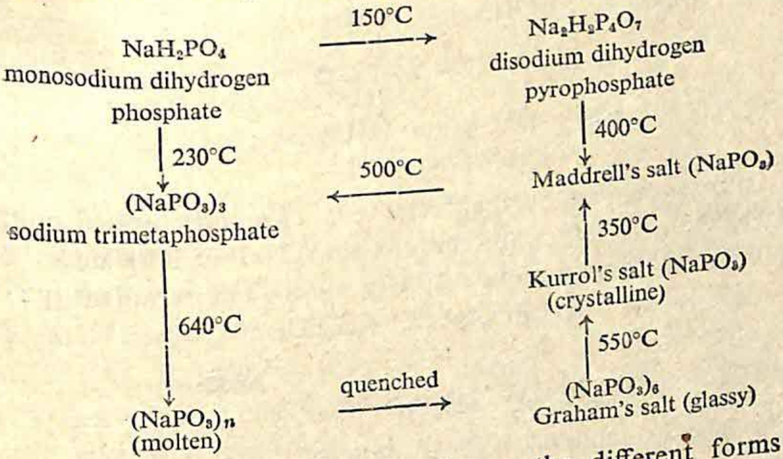
$$NaH_2PO_4 \rightarrow NaPO_3+H_2O\ ;$$
$$Na_2H_2P_2O_7 \rightarrow 2NaPO_3+H_2O.$$

The mixed sodium-ammonium orthophosphate, $NaNH_4HPO_4$, known as microcosmic salt, yields $NaPO_3$ on heating :

$$NaNH_4HPO_4 = NaPO_3+NH_3+H_2O.$$

Sodium hexametaphosphate, generally represented as $(NaPO_3)_6$, is used as a water-softener and is commercially known as *calgon*.

Action of heat on NaH_2PO_4 : Different types of metaphosphates are obtained on heating NaH_2PO_4 under different conditions :

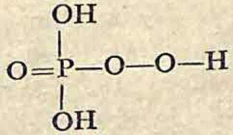


Kurrol's salt and Maddrell's salt are the different forms of $NaPO_3$. Sodium trimetaphosphate also exists in three polymorphic forms, depending on the temperatures to which the molten $(NaPO_3)_n$ is subjected to.

Peroxyphosphoric acids : Phosphorus forms two *peroxyphosphoric acids* or *perphosphoric acids*. The peroxymonophosphoric acid is prepared by reacting P_2O_5 with cold 30% H_2O_2 :

$$P_2O_5+2H_2O_2+H_2O=2H_3PO_5.$$

Structurally, it may be visualised to be formed by the replacement of one hydrogen of the H_2O_2 molecule by the H_2PO_3 group :

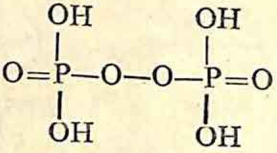


$$O=\overset{\displaystyle OH}{\underset{\displaystyle OH}{P}}—O—O—H$$

Permonophosphoric acid

It is a strong oxidising agent which liberates iodine instantaneously from an acid solution of an iodide. It is also obtained as the first product of hydrolysis of perdiphosphoric acid, $H_4P_2O_8$. It is rather unstable and hydrolyses into H_3PO_4 and H_2O_2. It is stored as alkali metal salts.

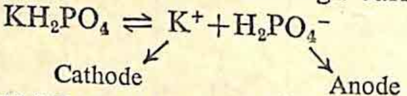
Perdiphosphoric acid : Structurally, it may be visualised as obtained from H_2O_2 by the replacement of both the hydrogens of H_2O_2 by two H_2PO_3 groups :



$$O{=}\underset{\displaystyle OH}{\overset{\displaystyle OH}{P}}{-}O{-}O{-}\underset{\displaystyle OH}{\overset{\displaystyle OH}{P}}{=}O$$

perdiphosphoric acid

This is best obtained by the electrolysis of a concentrated solution of NaH_2PO_4 or KH_2PO_4 (containing some NaF or KF) under cold conditions, using platinum electrodes and high current density :



$$KH_2PO_4 \rightleftharpoons \underset{\text{Cathode}}{\overset{}{K^+}}\swarrow + \searrow\underset{\text{Anode}}{H_2PO_4^-}$$

$$2H_2PO_4^- \rightarrow H_4P_2O_8 + 2e$$

This is an example of *anodic oxidation.*

This compound also is a strong oxidising agent. It liberates iodine from acidified iodide solution and oxidises Mn^{+2} to Mn^{+3} in acid solutions. It hydrolyses in two steps :

$$H_4P_2O_8 + H_2O = H_3PO_5 + H_3PO_4 ;$$
$$H_3PO_5 + H_2O = H_3PO_4 + H_2O_2.$$

Halides and oxyhalides of phosphorus : The following are the well-known halides of phosphorus :

Type formulae :	PX_3	PX_5
	(X=F, Cl, Br, I)	(X=F, Cl, Br)

The trihalides, PX_3.

Methods of preparation : PCl_3 and PBr_3 are conveniently prepared by reacting elemental phosphorus (red P) with the appropriate halogens, care being taken to avoid excess of the latter. PF_3 is generally prepared from PCl_3 by treatment with a fluoride like AsF_3, SbF_3 or HF, while PI_3 is prepared by dissolving white phosphorus and iodine (in the ratio 1 : 3) in carbon disulphide and cooling.

Properties :

Phosphorus trifluoride, PF_3 : PF_3 is a gas at ordinary temperatures and a liquid below −95°C. It is hydrolysed very slowly by water, but caustic alkalis hydrolyse it very rapidly, leading to the formation of the salts of phosphoric acid.

Phosphorus trichloride, PCl_3 : It is a fuming liquid, boiling at 76°C. It is violently hydrolysed by water to phosphorous acid. When treated with concentrated sulphuric acid, it gives chlorosulphonic acid and metaphosphoric acid :

$$2H_2SO_4+PCl_3=HSO_3Cl+HPO_3+SO_2+2HCl.$$

On reaction with SO_3, it produces phosphoryl chloride : $PCl_3+SO_3=POCl_3+SO_2$.

Thionyl chloride ($SOCl_2$) reacts with PCl_3 to form a mixture containing thiophosphoryl chloride ($PSCl_3$), phosphoryl chloride and phosphorus pentachloride : $3PCl_3+SOCl_2=PSCl_3+POCl_3+PCl_5$.

Phosporus tribromide, PBr_3 : It is a liquid, freezing at 40°C and boiling at 175.3°C. It resembles PCl_3 in most of its chemical properties.

PI_3 : It is a red crystalline solid, melting at 61°C and resembles PCl_3 and PBr_3 in most of its chemical properties.

The pentahalides, PX_5.

Phosphorous pentafluoride, PF_5 : This is generally obtained by treating PCl_5 with AsF_3 : $3PCl_5+5AsF_3=3PF_5+5AsCl_3$

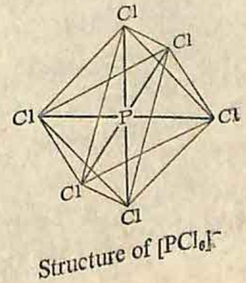
It is a gas which fumes in air. It is hydrolysed to H_3PO_4 by water : $2PF_5+8H_2O=2H_3PO_4+10HF$.

With calculated quantity of water, it forms phosphorus oxyfluoride, POF_3.

This is the stablest of the three pentahalides of phosphorus and possesses a trigonal bipyramidal structure similar to PCl_5 (See vol. I p. 150).

Phosphorus pentachloride, PCl_5 : This is conveniently obtained by reacting PCl_3 and chlorine : $PCl_3+Cl_2=PCl_5$.

It is a yellowish crystalline solid which sublimes at 160°C and melts at 167°C under the pressure of its own vapour. It fumes in moist air, and forms $POCl_3$ with a limited quantity of water, just like PF_5. It resembles PF_5 in most of its chemical properties and is completely hydrolysed to H_3PO_4 by excess of water. It is more reactive than PF_5.



Structure of $[PCl_6]^-$

In the crystalline solid state, phosphorus pentachloride is ionic and is composed of the $[PCl_4]^+$ cation and $[PCl_6]^-$ anion, and forms conducting solutions in nitrobenzene and acetonitrile (CH_3CN). $[PCl_6]^-$ have an octahedral structure as shown at page 155.

In the vapour state and in solution in non-polar solvents like benzene and carbon tetrachloride, it exists as discrete PCl_5 molecules. PCl_5 has a trigonal bipyramid structure similar to that of PF_5.

Phosphorus pentabromide, PBr_5 : It is prepared by the reaction of PBr_3 with Br_2 : $PBr_3+Br_2=PBr_5$. It is a rather unstable yellow solid, resembling PCl_5 in most of its chemical properties.

Phosphorus oxyhalides : Oxyhalides of pentavalent phosphorus, having the general formula POX_3 (X=F, Cl, Br), are well-known. Two other oxychlorides, pyrophosphoryl chloride ($P_2O_3Cl_4$) and octachlorotetraphosphoryldichloride ($P_4O_4Cl_{10}$) are also obtained by oxidising $POCl_3$ with NO_2. POI_3 is not known.

Phosphoryl fluoride or phosphorus oxyfluoride, POF_3 : This is obtained by the action of calculated quantity of water on phosphorus pentafluoride : $PF_5+H_2O=POF_3+2HF$.

It is a gas (b.p. $-40^\circ C$) with a pungent odour. It is slowly hydrolysed by cold water, the ultimate product being H_3PO_4 :

$$\begin{tikzcd} O=PF_3 \arrow[r, "H_2O"] & O=P(OH)F_2 \arrow[r, "H_2O"] & O=P(OH)_2F \arrow[d, "H_2O"] \\ & & \begin{array}{c} O=P(OH)_3 \\ (H_3PO_4) \end{array} \end{tikzcd}$$

Phosphoryl chloride or phosphorus oxychloride, $POCl_3$:

The compound is formed by the action of a limited quantity of water on PCl_5. But, the reaction is difficult to control and hence, it is best obtained by the reaction of boric acid or oxalic acid on PCl_5 :

$$3PCl_5+2B(OH)_3=3POCl_3+B_2O_3+6HCl\ ;$$
$$PCl_5+(COOH)_2=POCl_3+CO+CO_2+2HCl.$$

It is a clourless liquid, freezing at 0°C and boiling at 107°C. It is hydrolysed rapidly by water, yielding H_3PO_4 as the final product. It has a perceptible tendency to ionize as follows :

$$POCl_3 \rightleftharpoons [POCl_2]^+ + Cl^-.$$

This is manifested in the formation of complex compounds like $[POCl_2]^+ [SbCl_6]^-$, $[POCl_2]_2^{+2} [SnCl_6]^{2-}$ *etc.*

Phosphoryl bromide or phosphorus oxybromide, $POBr_3$:

This compound may be obtained from PBr_5 by methods similar to those used in the case of $POCl_3$. However, it is most conveniently obtained by reacting P_2O_5 with PBr_5 :

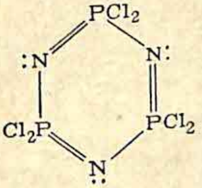
$$P_2O_5+3PBr_5=5POBr_3.$$

It is a solid, melting at 56°C and is similar to PCl_5 in all its properties.

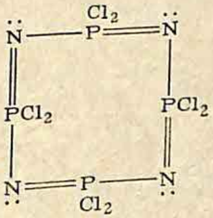
The PO_4^{3-} ion and the phosphoryl halides have the same mumber of electrons in the valence-shell of phosphorus, and hence they have similar distorted tetrahedral structures (see vol II, p. 152) with X—P—X bond angles of 103°.

Phosphorus chloronitrides.

Various products, having the empirical formula $PNCl_2$, are obtained when PCl_5 is heated with NH_4Cl at 130°C in a closed vessel or in an inert solvent like hexachloroethane (C_2Cl_6). These are called phosphorus chloronitrides. The two simplest products are the trimer $(PNCl_2)_3$ and the tetramer $(PNCl_2)_4$, which are found to have the structures I and II :



$(PNCl_2)_3$
I

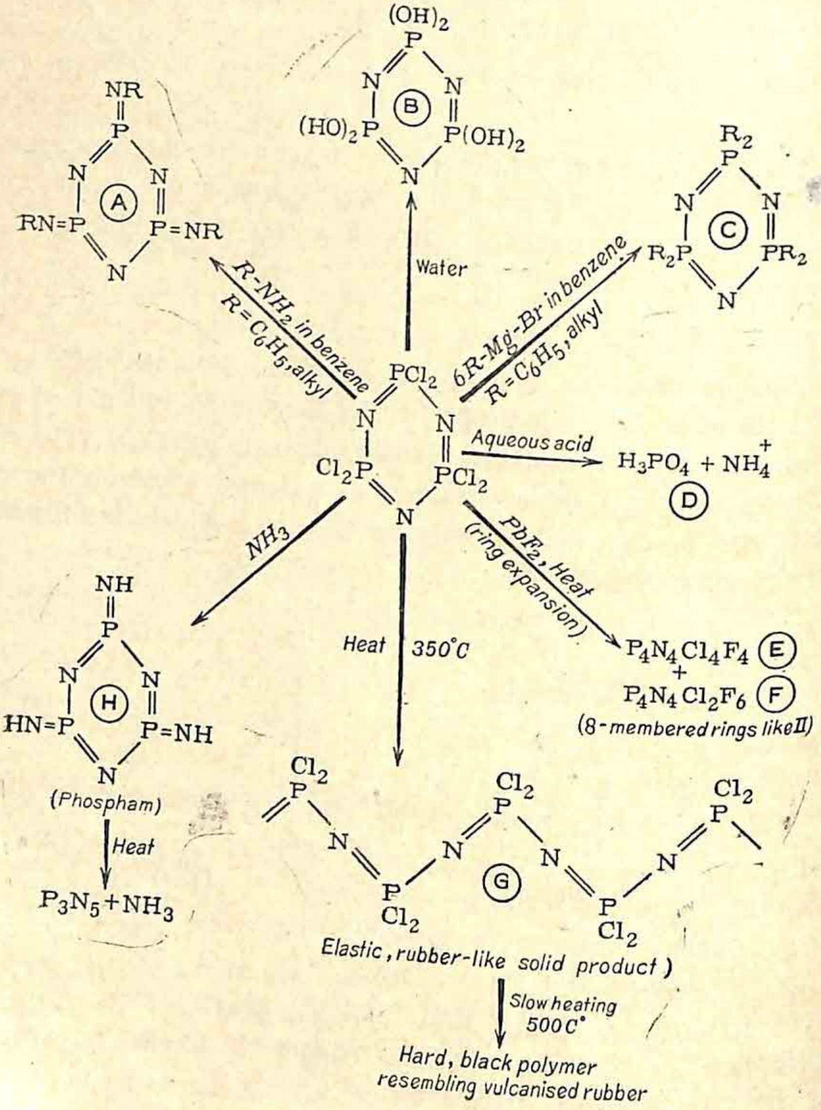


$(PNCl_2)_4$
II

It is apparent that (I) resembles benzene and (II) resembles cyclooctatetraene. From X-ray analyses of (I) and (II), it has been found that all P—N distances are the same and hence the formulae (I) and (II) are one of the different resonating forms, while the overall structure of each molecule must be a resonance-hybrid.

The chlorine atoms, attached to the phosphorus atoms, are reactive and undergo hydrolysis when they are replaced by OH groups. In this respect, the tetramer is more active than the trimer, and is hydrolysed by boiling water finally to the octahydroxy compound $[PN(OH)_2]_4$, which is remarkably stable.

The more important reactions of the trimer are given below :


(OH)₂P, N, N, (HO)₂P, P(OH)₂, N — B
NR, P, N, N, RN=P, P=NR, N — A
R₂P, N, N, R₂P, PR₂, N — C
Water
R-NH₂ in benzene R=C₆H₅, alkyl
6R-Mg-Br in benzene R=C₆H₅, alkyl
PCl₂, N, N, Cl₂P, PCl₂, N
Aqueous acid
H₃PO₄ + NH₄⁺ D
NH₃
PbF₂, Heat (ring expansion)
P₄N₄Cl₄F₄ E
+
P₄N₄Cl₂F₆ F
(8-membered rings likeII)
Heat 350°C
NH, P, N, N, HN=P, P=NH, N — H
(Phospham)
Heat
P₃N₅+NH₃
Cl₂P, N, P Cl₂, N, Cl₂P, N, P Cl₂, N, Cl₂P — G
Elastic, rubber-like solid product)
Slow heating 500C°
Hard, black polymer resembling vulcanised rubber

The product G is a rubber-like elastic solid known as *inorganic rubber*.

ARSENIC

Occurrence : Arsenic occurs rather widely in nature in combination with sulphur, iron and nickel. The chief ores from which arsenic is extracted are (i) Arsenical pyrites, FeAsS, (ii) Nickel glance, NiAsS, (iii) Realgar, As_2S_2 and (iv) Orpiment, As_2S_3.

Extraction : Arsenic is generally extracted by two different methods : (i) By heating arsenical pyrites at about 700°C out of contact with air : $FeAsS \longrightarrow FeS + As$.

Arsenic sublimes off at this temperature and is cooled on a cold surface.

(ii) Arsenical pyrites or Realgar, on roasting in air, forms As_2O_3 which is collected as a white sublimate : $4FeAsS + 3O_2 = 4FeS + 2As_2O_3$. This As_2O_3 is mixed with powdered charcoal and heated in a crucible : $As_2O_3 + 3C = 2As + 3CO$. Arsenic sublimes off and is collected as a sublimate.

Allotropic modifications of arsenic : As already stated, arsenic exists in three allotropic modifications, *viz*. yellow, grey and black arsenic, of which only grey arsenic is stable at ordinary temperatures. The yellow arsenic has a *cubic lattice*, whereas both the grey and the black varieties are *rhombic forms*. Some important properties of these three forms are tabulated below :

Property	Yellow Arsenic	Black Arsenic	Grey Arsenic
Colour	Yellow.	Black.	Steel grey with metallic lusture.
Structure	Cubic.	Rhombic.	Rhombic.
Stability at room temp.	Metastable.	Metastable.	Stable.
Density	3.98 gm/c.c.	4.6 gm/c.c.	5.73 gm/c.c.
Electrical conductivity	Non-conducting.	Non-conducting.	Feebly conducting.
Solubility in carbon disulphide	Soluble.	Insoluble.	Insoluble.

Metalloid nature of arsenic : Non-malleable nature, existence of allotropic forms and formation of oxyacids on reaction with nitric acid are the evidences of the non-metallic nature of arsenic. Oxides of arsenic are amphoteric in nature, being soluble in strong acids as well as in alkalis. These reactions clearly indicate the metallic as well as non-metallic character, *i.e. metalloid* character of arsenic.

The resemblances of arsenic with metals are exhibited in the following properties : The grey form has a metallic lusture and conducts electricity to some extent. It has a high density like metals. It forms alloys with many metals.

Thus, arsenic shows resemblance to both metals and non-metals and hence represents the metalloidal character.

Arsenic is rather inert at ordinary temperatures. It burns in air, forming fumes of As_2O_3. It reacts with halogens and sulphur, forming trihalides and trisulphide.

Since arsenic occurs below hydrogen in the electrochemical series, it does not react with dilute HCl and H_2SO_4 and even with dil. HNO_3. Hot, concentrated nitric acid oxidises arsenic to As_2O_5, which forms arsenic acid with water :

$$2As+10HNO_3=2H_3AsO_4+10NO_2+2H_2O.$$

Hot, concentrated H_2SO_4 oxidises arsenic to arsenious acid :

$$2As+3H_2SO_4=2H_3AsO_3+3SO_2.$$

On fusion with alkali, arsenic forms arsenites :

$$2As+6NaOH=2Na_3AsO_3+3H_2\uparrow.$$

Hydrides : The only well-established hydride of arsenic is arsine, AsH_3. Elemental arsenic does not combine directly with hydrogen and hence, AsH_3 is prepared by the reduction of a trivalent arsenic compound with nascent hydrogen generated by the action of zinc or magnesium and dil. HCl :

$$AsCl_3 + 6H = AsH_3 + 3HCl.$$

Pure AsH_3 is best obtained by reacting zinc arsenide with dil. H_2SO_4 :

$$Zn_3As_2+3H_2SO_4=2AsH_3\uparrow+3ZnSO_4.$$

It is a colourless gas, liquefying at −55°C and solidifying at −119°C.

It is a strong reducing agent and precipitates heavy metals from the solutions of their salts :

$$2AsH_3+6AgNO_3=6Ag\downarrow+As_2O_3+6HNO_3.$$

It is thermally unstable and is decomposed to the black metallic arsenic, which is the basis of the **Marsh test** for arsenic.

Unlike ammonia, AsH_3 has no basic character and is very little soluble in water.

Oxides : Two oxides of arsenic, the trioxide and the pentoxide, are well established.

Arsenic trioxide, As_4O_6 : This is formed (i) when arsenic is burnt in air, or (ii) by heating arsenical pyrites, FeAsS, in air :

$2FeAsS+5O_2=Fe_2O_3+2SO_2+As_2O_3$, and is collected as a white sublimate.

It is correctly represented as As_4O_6 and resembles P_4O_6 in most of its properties and structure.

It occurs in several forms, such as (i) amorphous form, (ii) octahedral form (crystalline) and (iii) monoclinic form (crystalline).

It is highly poisonous, the lethal dose is 50 mg. It forms arsenious acid with water : $As_2O_3+3H_2O=2H_3AsO_3$. It does not change into pentoxide even when heated in oxygen, but is oxidised to the latter when heated with concentrated nitric acid or hydrogen peroxide :

$$As_2O_3+HNO_3 \rightarrow As_2O_5 ;$$
$$As_2O_3+2H_2O_2 \rightarrow As_2O_5+2H_2O.$$

It is an amphoteric oxide which forms $As_2(SO_4)_3$ with concentrated sulphuric acid :

$$As_2O_3+3H_2SO_4=As_2(SO_4)_3+3H_2O.$$

With alkali, it forms arsenite :

$$As_2O_3+6NaOH=2Na_3AsO_3+3H_2O.$$

As_2O_3 and arsenites are fairly strong reducing agents which reduce iodine to iodide and ferric iron to the ferrous state :

$$As_2O_3+2\,I_2+2H_2O=2AsO_4^{3-}+4I^-+4H^+ ;$$
$$AsO_3^{3-}+2Fe^{+3}+H_2O=AsO_4^{3-}+2Fe^{+2}+2H^+.$$

Arsenic pentoxide, As_4O_{10} or As_2O_5 : This is obtained by the oxidation of As_2O_3 by concentrated nitric acid to arsenic acid, H_3AsO_4, and subsequent dehydration of the H_3AsO_4 to As_2O_5 by heating :

$$As_2O_3+4HNO_3+H_2O=2H_3AsO_4+4NO_2 ;$$
$$2H_3AsO_4=As_2O_5+3H_2O.$$

Unlike P_2O_5, As_2O_5 is dissociated to As_2O_3 and O_2 on heating. It is a white solid which is distinctly acidic in character. It dissolves in water, yielding arsenic acid, H_3AsO_4 :

$$As_2O_5+3H_2O=2H_3AsO_4.$$

It is an oxidising agent and liberates chlorine from HCl and reacts with PCl_5, forming $POCl_3$ and liberating chlorine :

$$As_2O_5+10HCl=2AsCl_3+2Cl_2+5H_2O\ ;$$
$$As_2O_5+5PCl_5=5POCl_3+2AsCl_3+2Cl_2.$$

Oxyacids of arsenic : Two oxyacids of arsenic are well established. These are H_3AsO_3 or $HAsO_2$ and H_3AsO_4.

Arsenious acid, H_3AsO_3 : It can be obtained by reacting As_2O_3 with water : $As_2O_3+3H_2O=2H_3AsO_3$. It is a weak acid, known only in solution. It is a tribasic acid and on complete neutralisation with NaOH forms Na_3AsO_3. It also forms organic esters like As $(OR)_3$, where R is an alkyl group.

Arsenic acid, H_3AsO_4 (orthoarsenic acid) : It is conveniently obtained by dissolving As_2O_3 in conc. HNO_3 and concentrating the solution. On cooling, the crystals of H_3AsO_4 separate out.

On heating to 450°C, it is dehydrated into As_2O_5 :

$$2H_3AsO_4=As_2O_5+3H_2O.$$

It is a fairly strong tribasic acid like H_3PO_4 and is much stronger than arseneous acid. Meta $(HAsO_3)$ and pyroarsenic acids $(H_4As_2O_7)$ are also known, but they are unstable and change into the orthoarsenic acid.

Ortho, meta and pyroarsenates of many metals are well-known, and are isomorphous with the corresponding phosphates.

Heat treatment of NaH_2AsO_4 (monosodium dihydrogen arsenate) yields several products :

$$\begin{tikzcd}
\begin{array}{c} NaH_2AsO_4 \\ \text{sodium dihydrogen} \\ \text{arsenate} \end{array} \arrow[r, "90^\circ C"] & \begin{array}{c} Na_2H_2As_2O_7 \\ \text{disodium dihydrogen} \\ \text{pyroarsenate} \end{array} \arrow[r, "135^\circ C"] & \begin{array}{c} Na_3H_2As_3O_{10} \\ \text{triarsenate} \end{array} \arrow[d, "230^\circ C"] \\
 & & \begin{array}{c} (NaAsO_3)_n \\ \text{meta-arsenate} \\ \text{(polymerised)} \end{array}
\end{tikzcd}$$

Halides of arsenic : All the trihalides of the type AsX_3 (X=F, Cl, Br and I) are known. The only known pentahalide is AsF_5.

All the trihalides can be prepared by the direct reaction of arsenic with the halogen :

$2As+3X_2=2AsX_3$ (where X=F, Cl, Br and I). AsF_3, $AsCl_3$, $AsBr_3$ and AsI_3 are all liquids at ordinary temperatures.

Arsenic trichloride, $AsCl_3$: Of all the trihalides, arsenic trichloride is of some importance. It is generally prepared by heating As_2O_3 with HCl : $As_2O_3+6HCl=2AsCl_3+3H_2O$.

Arsenic trichloride is a heavy and viscous liquid with a m.p. of −18°C and a b.p. of 122°C. It resembles PCl_3 in its structure and in most of its chemical properties. However its hydrolysis by water to the arseneous acid is reversible :

$$AsCl_3+3H_2O \rightleftharpoons H_3AsO_3+3HCl$$

Arsenic pentafluoride, AsF_5, is obtained by heating together AsF_3, bromine and antimony pentafluoride :

$$AsF_3+Br_2+2SbF_5=AsF_5+2SbBrF_4.$$

Sulphides : Three sulphides of arsenic, *viz.* the disulphide (As_2S_2), the trisulphide (As_2S_3) and the pentasulphide (As_2S_5) are well-established.

Arsenic disulphide, As_2S_2, occurs in nature as the mineral **Realgar** and is obtained by strongly heating a mixture of iron pyrites and arsenical pyrites : $2FeS_2+2FeAsS=As_2S_2+4FeS$.

It is an orange-red solid and burns in air with a blue flame :

$$2As_2S_2+7O_2=2As_2O_3+4SO_2.$$

Arsenic trisulphide, As_2S_3 : It is found in nature as the mineral **orpiment.** It may be prepared by (i) heating arsenic and sulphur in 2 : 3 proportions, or (ii) by passing H_2S through an acidified solution of any trivalent arsenic salt : $2As^{+3}+3S^{2-}=As_2S_3\downarrow$.

It is a yellow solid, insoluble in water and in dilute acids, but is soluble in alkalis, yielding thioarsenites and arsenites :

$$As_2S_3+6NaOH=\underset{\text{sodium thioarsenite}}{Na_3AsS_3}+Na_3AsO_3+3H_2O.$$

It dissolves in yellow ammonium sulphide, forming thioarsenates :

$$As_2S_3+(NH_4)_2S_2\rightarrow(NH_4)_3AsS_4+S\downarrow.$$

Thioarsenites and thioarsenates are soluble in water. The thioarsenates, on treatment with conc. HCl, produce As_2S_5 which is precipitated : $2(NH_4)_3AsS_4+6HCl=As_2S_5\downarrow+3H_2S+6NH_4Cl$. Thioarsenites precipitate As_2S_3 on treatment with HCl :

$$2Na_3AsS_3+6HCl=As_2S_3+3H_2S+6NaCl.$$

Arsenic pentasulphide, As_2S_5 : It may be conveniently prepared by fusing powdered As_2S_3 and sulphur in 1 : 2 proportions : $As_2S_3+2S=As_2S_5$. It can also be prepared by decomposing a thioarsenate by conc. HCl (see above).

It is an orange solid which dissolves in alkalis, like As_2S_3, forming thioarsenates and arsenates :

$4As_2S_5+24NaOH=5Na_3AsS_4+3Na_3AsO_4+12H_2O$. Just like As_2S_3 it forms thioarsenate with alkali sulphides (or ammonium sulphide) : $As_2S_5+(NH_4)_2S_2 \rightarrow (NH_4)_3AsS_4+3S\downarrow$.

ANTIMONY

Occurrence : Antimony occurs in nature chiefly as the crystalline black ore **stibnite,** containing Sb_2S_3. In small quantities, antimony also occurs in the free state.

Extraction : Antimony is generally obtained by heating the stibnite ore with scrap iron, when both metallic antimony and iron sulphide formed remain in the molten state. The iron sulphide, being much lighter, floats on the surface and is easily separated.

$$Sb_2S_3+3Fe=2Sb+3FeS.$$

Antimony is also extracted from low grade sulphide ores, first by roasting it with half its weight of coke in a limited supply of air, when Sb_2S_3 is mostly converted into volatile Sb_2O_3 which is obtained as a white sublimate : $2Sb_2S_3+9O_2=2Sb_2O_3+6SO_2$. The antimony trioxide is then heated with charcoal in a crucible, when it is reduced to antimony : $Sb_2O_3+3C=2Sb+3CO$.

Allotropic modifications of antimony : Like phosphorus and arsenic, antimony also exists in three different allotropic modifications, *viz*. metallic antimony, α-antimony and explosive antimony, of which, the metallic form is stable. Some important properties of these three forms are tabulated below : (*see table at p*. 165).

Metallic antimony exhibits a stronger metallic character than arsenic. Like arsenic, antimony is inert in a dry atmosphere at ordinary temperatures. It burns in oxygen, forming Sb_2O_3 and Sb_2O_4. It burns in chlorine, yielding $SbCl_3$ at first, and $SbCl_5$ on prolonged heating. It combines with phosphorus and sulphur on heating to form phosphides and sulphides. Since its position is below that of hydrogen in the electrochemical series, pure antimony

Property	explosive antimony	Black β-antimony.	Metallic antimony
Colour	Yellow	Black	Silver-grey, with a metallic lusture.
Structure	Crystalline (cubic)	Amorphous	Crystalline (rhombohedral).
Stability at room temperature	Unstable	Metastable	Stable
Solubility in CS_2	Soluble	Insoluble	Insoluble
Density gm/c.c.	—	5.25—6.3	6.7
Electrical conductivity	Almost non-conducting	Almost non-conducting	Feeble conductor of electricity.
Method of preparation	By the action of ozone on liquid stibine at −90°C.	By the slow electrolysis of an HCl solution of $SbCl_3$, using Pt-cathode and antimony anode.	Fused metal cooled slowly.

is not attacked by dilute acids. However, it is attacked by hot conc. H_2SO_4, forming $Sb_2(SO_4)_3$ and liberating SO_2 :

$$2Sb+6H_2SO_4=Sb_2(SO_4)_3+3SO_2+6H_2O.$$

On heating with concentrated HNO_3, antimony is oxidised to Sb_2O_5 which reacts with water and forms antimonic acid, H_3SbO_4 :

$$2Sb+10HNO_3=Sb_2O_5+10NO_2+5H_2O\ ;$$
$$Sb_2O_5+3H_2O=2H_3SbO_4.$$

Like arsenic, it burns in chlorine, forming $SbCl_3$ which is converted into $SbCl_5$ on prolonged reaction :

$$2Sb+3Cl_2=2SbCl_3\ ;\ SbCl_3+Cl_2=SbCl_5.$$

Compound of antimony.

Antimony hydride, SbH_3 (stibine) : Like arsine, (AsH_3), stibine is also prepared by the reduction of trivalent antimony compounds by nascent hydrogen :

$$SbCl_3+3Zn+3H_2SO_4=SbH_3\uparrow+3ZnSO_4+3HCl.$$

It is a colourless poisonous gas, even more unstable than AsH_3, and decomposes into black antimony and hydrogen even at ordinary temperatures : $2SbH_3 = 2Sb + 3H_2\uparrow$. It is thus a strong reducing agent, even stronger than AsH_3.

Its reaction with silver nitrate solution is similar to the reaction of arsine :

$$2SbH_3+12AgNO_3+3H_2O=12Ag\downarrow+Sb_2O_3+12HNO_3.$$

SbH_3 burns in air, the fumes of Sb_2O_3 being formed.

Oxides : Three oxides of antimony, *viz*. Sb_4O_6, Sb_2O_4 and Sb_2O_5 are well-known. (Arsenic does not form the textroxide analogue of Sb_2O_4.)

Antimony trioxide, Sb_2O_3 or Sb_4O_6 : Just like As_2O_3, it is obtained by burning antimony in air, or by burning SbH_3 in air. It melts at 650°C and its vapour density corresponds to the formula Sb_4O_6.

It is a white powder, sparingly soluble in water, but soluble in both strong acids and alkalis. With strong acids like conc. HCl, H_2SO_4 and HNO_3, it yields the corresponding trivalent salts and water :

$$Sb_4O_6+12HCl=4SbCl_3+6H_2O\ ;$$
$$Sb_4O_6+12HNO_3=4Sb(NO_3)_3+6H_2O\ ;$$
$$Sb_4O_6+6H_2SO_4=2Sb_2(SO_4)_3+6H_2O.$$

It dissolves in a boiling solution of potassium hydrogen tartarate (as well as in tartaric acid), forming *tartar emetic*, $K(SbO)C_4H_4O_6$:

$$2KHC_4H_4O_6+Sb_2O_3=2K(SbO)C_4H_4O_6+H_2O.$$

The structure of Sb_2O_3 is similar to that of As_4O_6 or P_4O_6.

Antimony tetroxide, Sb_2O_4 : This may be obtained by the thermal decomposition of Sb_2O_5 above 440°C :

$$2Sb_2O_5=2Sb_2O_4+O_2.$$

It is a white solid, turning yellow on heating, which regains the white colour on cooling. On strong heating, it is decomposed to the trioxide : $2Sb_2O_4=2Sb_2O_3+O_2$. It is insoluble in water and yields hypoantimonate on fusion with an alkali :

$$Sb_2O_4+2NaOH=Na_2Sb_2O_5+H_2O.$$

Antimony pentoxide, Sb_2O_5 or Sb_4O_{10} : It is conveniently prepared by heating the white residue ($HSbO_3$), left after heating antimony metal, repeatedly with conc. HNO_3 :

$$2HSbO_3\xrightarrow{\text{heat}}Sb_2O_5+H_2O.$$

It is a yellow solid. Above 440°C, it decomposes to Sb_2O_4, which forms Sb_2O_3 on further heating. It is an acidic oxide, and though sparingly soluble in water, its aqueous solution is acidic in nature. It is a mild oxidising agent, and a concentrated HCl solution of Sb_2O_5 liberates iodine from KI :

$$Sb_2O_5+4I^-+10H^+=2Sb^{+3}+2I_2+5H_2O.$$

Oxyacids of antimony : Antimonous acid (corresponding to the arseneous acid) is not known, but the textroxide yields antimonites on their diosslution in alkali. Antimonic acid is formulated as $HSb(OH)_6$; but, it has not been isolated in the solid state. Its Li, Na and K-salts, $MSb(OH)_6$, are obtained by dissolving Sb_2O_5 in strong alkalis :

$$Sb_2O_5+2NaOH+5H_2O=2Na[Sb(OH)_6].$$

Halides : Antimony forms both tri and pentahalides, corresponding to the general formulae SbX_3 (X=F, Cl, Br & I) and SbX_5 (X=F and Cl).

Trihalides, SbX_3 : $SbCl_3$, $SbBr_3$ and SbI_3 are obtained by the direct reaction between antimony and the appropriate halogen (sometimes in CS_2 or CCl_4 medium) :

$$2Sb+3X_2=2SbX_3\ (X=Cl,Br,I).$$

SbF_3 is prepared by reacting Sb_4O_6 with HF :

$$Sb_4O_6+12HF=4SbF_3+6H_2O.$$

$SbCl_3$ is a crystalline white solid. All the trihalides are extensively hydrolysed in water and the oxyhalides, SbOX, are precipitated down : $SbX_3+H_2O=SbOX+2HX$ (X=F, Cl, Br, I).

The precipitate redissolves on addition of HX and is also soluble in tartaric acid. On boiling with excess water, Sb_2O_3 is formed.

Pentahalides, SbX_5 (X=F,Cl) : These are obtained by the prolonged action of the halogens on SbX_3 :

$$SbX_3+X_2=SbX_5\ (X=F,Cl).$$

$SbCl_5$ is a yellow liquid, boiling at 140°C and fuming strongly in air. It is hydrolysed by water to Sb_2O_5 :

$$2SbCl_5+5H_2O=Sb_2O_5+10HCl.$$

Sulphides : Two sulphides of antimony are known—Sb_2S_3 and Sb_2S_5.

Antimony trisulphide, Sb_2S_3 : It is obtained as an *orange-red precipitate* when H_2S is passed through a dilute hydrochloric acid solution of a soluble antimony salt like $SbCl_3$:

$$2SbCl_3+3H_2S=Sb_2S_3\downarrow+6HCl.$$

It is converted into the black rhombic form on heating to 200°C in an inert atmosphere. Just like As_2S_3, it is insoluble in dilute acids, but dissolves in hot conc. acids :

$$Sb_2S_3+6HCl=2SbCl_3+3H_2S.$$

Like As_2S_3, Sb_2S_3 reacts with strong alkalis to form thiontimonites (SbS_3^{3-}) and antimonites (SbO_3^{3-}). It reacts with yellow ammonium sulphide to form ammonium thioantimonate :

$$Sb_2S_3+3(NH_4)_2S+2S=2(NH_4)_3SbS_4.$$

Antimony pentasulphide, Sb_2S_5 : It is obtained by passing H_2S through a dilute HCl solution of $SbCl_5$: $2SbCl_5+5H_2S=Sb_2S_5+10HCl$. Sb_2S_5 reacts with alkali sulphides to form thioantimonates : $Sb_2S_5+3Na_2S=2Na_3SbS_4$. It is an orange-red solid.

BISMUTH

Occurrence : The important ores of bismuth are *bismuth glance*, Bi_2S_3, and the oxide, bismuth orchre, Bi_2O_3. It also occurs in the native state.

Extraction (from the sulphide ore) : The sulphide ore is roasted in air, when it is converted into the oxide : $2Bi_2S_3+9O_2=2Bi_2O_3+6SO_2$. The oxide is then reduced by heating with carbon to yield the crude metal : $Bi_2O_3+3C=2Bi+3CO$.
The crude metal is then fused with nitre, when most of the impurities are oxidised, leaving pure bismuth metal.

Bismuth is a true metal, and unlike P, As and Sb, it does not exist in allotropic modifications. It is a lustrous silvery metal, which is brittle and boils at 271.3°C. It conducts electricity well.

Like arsenic and antimony, bismuth is rather inert and is not tarnished in open air. On heating in air, it forms Bi_2O_3 :

$$4Bi+3O_2=2Bi_2O_3.$$

It combines with fluorine, chlorine and bromine, forming the trihalides : $2Bi+3X_2=2BiX_3$, (X=F, Cl, Br).
It is not attacked by dil. HCl and H_2SO_4 and not even by conc. HCl. But, it dissolves readily in dil. HNO_3 :

$$2Bi+8HNO_3=2Bi(NO_3)_3+2NO+4H_2O.$$

When heated with conc. H_2SO_4, bismuth is converted into bismuth sulphate, and SO_2 is liberated :

$$2Bi+6H_2SO_4=Bi_2(SO_4)_3+3SO_2+6H_2O.$$

Compounds of bismuth.

Bismuth hydride, BiH_3 (bismuthine) : BiH_3 is obtained in minute quantities when an alloy of magnesium and bismuth is treated with dilute HCl. It can be detected by using a radioactive isotope of bismuth in the alloy. It has a transient existence. It is very unstable, much more so than AsH_3 and SbH_3.

Oxides of bismuth : Three oxides of bismuth are well-known, *viz.* Bi_2O_3 (trioxide), Bi_2O_4 (tetroxide) and the pentoxide, Bi_2O_5.

Bismuth trioxide, Bi_2O_3 : It is a yellow powder, obtained either by heating metallic bismuth in air or, by strongly heating $Bi_2(CO_3)_3$ or any other salt of bismuth : $Bi_2(CO_3)_3=Bi_2O_3+3CO$; $4Bi(NO_3)_3=2Bi_2O_3+12NO_2+3O_2$.

It is rather amphoteric in nature and reacts with alkalis and acids, forming bismuthites and bismuth salts respectively :

$$Bi_2O_3+6NaOH=2Na_3BiO_3+3H_2O.$$

$$Bi_2O_3+6HCl=2BiCl_3+3H_2O.$$

Bismuth tetroxide, Bi_2O_4 : Bi_2O_4 is prepared by passing chlorine through a suspension of the trioxide in dil. KOH :

$$Bi_2O_3+Cl_2+H_2O=Bi_2O_4+2HCl.$$

It is scarlet-red powder.

Bismuth pentoxide, Bi_2O_5 : When chlorine is passed through a suspension of Bi_2O_3 in water for a long time, a scarlet-red ppt. of $KBiO_3$ is obtained. This potassium metabismuthate, $KBiO_3$, is first washed with water and then boiled with dilute nitric acid, when it is converted to the scarlet-red metabismuthic acid, $HBiO_3$. This is then dehydrated over concentrated H_2SO_4, and bismuth pentoxide is thus obtained :

$$2HBiO_3 \xrightarrow[\text{(conc. } H_2SO_4)]{-H_2O} Bi_2O_5.$$

It is a brown ammorphous solid. When heated above 120°C, it decomposes into Bi_2O_3 and oxygen : $Bi_2O_5=Bi_2O_3+O_2$. It is a fairly strong oxidising agent and reacts with HCl to produce $BiCl_3$ and liberate chlorine : $Bi_2O_5+10HCl=2BiCl_3+2Cl_2\uparrow+5H_2O$. With sulphuric acid, it forms $Bi_2(SO_4)_3$ and liberates oxygen :

$$Bi_2O_5+3H_2SO_4=Bi_2(SO_4)_3+O_2\uparrow+3H_2O.$$

test for nitrite confirms the presence of nitrate, from which this nitrite is derived.

Test for phosphorus : Since most phosphorus compounds and all oxyacids (and oxyanions) of phosphorus are oxidised to the orthophosphate on boiling with nitric acid, phosphorus is best detected as the orthophosphate ion, $PO^{3}{}_{4}{}^{-}$. When a solution containing phosphate (or other oxyanions of phosphorus) is heated with excess nitric acid, and ammonium molybdate solution is added to it, a canary yellow precipitate of ammonium phosphomolybdate is deposited :

$$12\,(NH_4)_2\,MoO_4+Na_2HPO_4+23HNO_3=(NH_4)_3[PMo_{12}O_{40}]\downarrow$$
$$+2NaNO_3+21NH_4NO_3+12H_2O$$

Arsenate, AsO_4^{3-}, gives similar yellow precipitate of ammonium arsenomolybdate.

The presence of PO_4^{3-} in presence of AsO_4^{3-} can be established by using a solution of ammonium molybdate in 15% tartaric acid, in which the arsenomolybdate is soluble but the phosphomolybdate is insoluble.

Determination of Phosphate (PO_4^{3-}) : Phosphate may be quantitatively precipitated as $Mg(NH_4)PO_4$ from a solution containing NH_4Cl and NH_4OH, by the addition of a slight excess of a $Mg(NO_3)_2$ solution. This precipitate of $Mg(NH_4)PO_4$ is filtered, washed free of Mg^{+2} and ignited to $Mg_2P_2O_7$ in a silica or porcelain crucible, cooled in a desiccator and weighed.

Test for arsenic : Arsenic (generally in its trivalent state) is detected in Gr. IIB of the analytical chemistry as As_2S_3, when H_2S is passed through a solution of an arsenic compound in dil. HCl :

$$2AsCl_3+3H_2S=\underset{\text{yellow}}{As_2S_3}\downarrow+6HCl.$$

Even arsenites and arsenates are also precipitated as As_2S_3 on prolonged treatment with H_2S. This As_2S_3 is then converted into the soluble thioarsenate by treating with yellow ammonium sulphide solution and separated from the Gr. IIA sulphides. It is then filtered and As_2S_3 is reprecipitated with concentrated HCl. The As_2S_3 is then converted to arsenate, AsO_4^{3-}, by heating with NH_4OH and H_2O_2 and treated with magnesia mixture ($MgCl_2+NH_4Cl+NH_4OH$), when a crystalline white precipitate of $Mg(NH_4)AsO_4$ confirms the presence of arsenic.

Traces of arsenic is efficiently detected by the Marsh test, which is based on the formation of volatile AsH_3 and its thermal decomposition into the black mirror of elemental arsenic :

$$2As^{+3}+6H^{+}+3Zn=2AsH_3+3Zn^{+2}\ ;$$
$$2AsH_3 \rightarrow \underset{\text{black mirror}}{2As}+3H_2\uparrow .$$

Determination of arsenic : Any compound of arsenic can easily be converted into either arsenite or arsenate, and arsenic is generally estimated either as arsenite or arsenate.

Arsenites are conveniently ditermined by titrating with a standard iodine solution at a pH$\sim$8 (maintained by the presence of $NaHCO_3$ in the reaction medium, which consumes up the H^+ ions generated), using starch as indicator :

$$AsO_3^{3-}+I_2+H_2O=AsO_4^{3-}+2I^-+2H^+.$$

Arsenates are determined iodometrically in acid solutions by treating the solution containing arsenate with an excess of KI and titrating the liberated iodine with a standard thiosulphate solution, using starch as indicator :

$$AsO_4^{3-}+2H^++2I^-=AsO_3^{3-}+I_2+H_2O.$$
$$I_2+2Na_2S_2O_3=Na_2S_4O_6+2NaI.$$

Test for antimony : Antimony may be detected as the orange Sb_2S_3, by passing H_2S through a dilute HCl solution containing antimony : $2SbCl_3+3H_2S\rightarrow \underset{\text{orange ppt.}}{Sb_2S_3\downarrow}+6HCl.$

It is soluble in yellow ammonium sulphide and hence, is separated from the Gr. IIA sulphides (HgS, PbS, CuS, Bi_2S_3, CdS) by warming with yellow ammonium sulphide and subsequent filtration, when antimony (along with arsenic and tin) goes into the filtrate :

$$Sb_2S_3+3(NH_4)_2S+2S\rightarrow \underset{\text{soluble}}{2(NH_4)_3SbS_4}.$$

When this solution containing antimony (as thio-antimonate) is acidified with conc. HCl, antimony comes in the solution as $H[SbCl_6]$ (As_2S_3 is not dissolved). If clean, shiny iron nails are dropped into this solution containing $H[SbCl_6]$, black metallic antimony is slowly deposited on the iron nails, confirming the presence of antimony. This happens because antimony occurs below iron in the electrochemical series.

Determination of antimony : When present in the +3 oxidation state as Sb^{+3} or as SbO_2^-, it can be estimated iodimetrically as iodine can oxidise SbO_2^- to SbO_3^- (i.e. Sb^{+3} to Sb^{+5}) quantitatively. The solution containing antimony (to be estimated) is treated with a measured excess of standard iodine solution (in a carbon dioxide atmosphere) and the excess iodine is back titrated with a standard thiosulphate solution, using starch as indicator :

$$SbO_2^- + I_2 + H_2O = SbO_3^- + 2HI.$$

$$I_2 + 2Na_2S_2O_3 = Na_2S_4O_6 + 2NaI.$$

Test for bismuth : On passing H_2S through a dilute HCl solution of a bismuth compound, Bi_2S_3 is precipitated in Gr. II (of analytical chemistry) as a dark brown precipitate. This precipitate is insoluble in yellow ammonium sulphide, but soluble in dilute nitric acid. When treated with an excess of alkaline stannite ($SnCl_2$ soln. treated with excess of NaOH soln.), this solution deposits black precepitate of bismuth metal.

Any salt of bismuth in acid solution, yields a white precipitate of BiOCl, on being added to a large volume of water. This ppt. of BiOCl is not soluble in oxalic acid (distinction from tin) or tartaric acid (difference from antimony), but is soluble in dil. HCl, HNO_3 and H_2SO_4.

CHAPTER XVII

GROUP VIB ELEMENTS : THE OXYGEN FAMILY

The group VIB of the Periodic Table consists of the elements oxygen, sulphur, selenium, tellurium and polonium. They are also called the *chalcogens*, meaning the ore-forming elements, because, most of the ores of metals occur in nature as oxides or sulphides. There is practically no resemblence between the metallic elements of Gr VIA (chromium, molybdenum, tungsten and uranium) and these non-melals of VIB.

Oxygen is the most abundant element, and in the combined state, constitutes about 47% of the earth's crust. Large amount of oxygen occurs in the free state in the atmosphere (~21% by volume). As water, it constitutes almost 90% of all the oceans. Sulphur is also fairly abundant and occurs to the tune of ~0.05% of the earth's crust. Selenium, tellurium and polonium are rather rare and occur in the earths crust to the extent of only 10^{-7}, 10^{-7} and 10^{-14} per cents respectively. It is quite clear that polonium is very rare. It is a member of the *Thorium and the Uranium series* and is an α-emitter (See Vol. I pages 204-206). Its chemistry becomes complicated due to its intense α-activity under all conditions, and we will give polonium less importance in our discussion, when we disscuss the behaviour of the individual elements as members of this group.

All the elements of this group are '*p*'*-block* elements with ns^2np^4 configuration in their *valence shells*. The regular variation of the important physical and chemical properties with atomic number is well-reflected in this group.

Some more important characteristics of the Gr VIB elements are given in table 17.1.

Variation in physical states of occurrence and the allotropic modifications : Like the elements of the preceding group (Gr. VB), these elements exhibit a gradual transition in their states of natural occurrence. Oxygen is a gaseous element which can be liquefied at −183°C. The next member sulphur is a rather soft and comparatively low-melting solid, vaporising at 444·6°C. Selenium, tellurium and polonium are all solid substances and are much harder than sulphur. Among the elements of this group, the M.P.s.

TABLE 17·1

Properties	Oxygen	Sulphur	Selenium	Tellurium	Polonium
Atomic number	8	16	34	52	84
Electronic configuration	$\boxed{\text{He}}\ 2s^2 2p^4$	$\boxed{\text{Ne}}\ 3s^2 3p^4$	$\boxed{\text{Ar}}\ 4s^2 4p^4$	$\boxed{\text{Kr}}\ 5s^2 5p^4$	$\boxed{\text{Xe}}\ 5d^{10} 6s^2 6p^4$
Atomic weight	15.999	32.064	78.96	127.60	[210] (stable isotope)
Atomic volume of solid (c.c.)	14.00	15.50	16.50	20.50	22.7
Atomic radius (Å)	0.73	1.02	1.16	1.35	—
Density (of solid) gm/c.c.	1.14	2.07	4.79	6.24	[9.2]
Ionization potential (ev.)	13.61	10.36	9.75	9.10	—
Electronegativity (Pauling's scale)	3.5	2.5	2.4	2.1	2.0
Oxidation states	−2	−2, +2, +4, +6	−2, +2, +4, +6	−2, +2, +4, +6	+2, +4
M. P. (°C)	−218.8	119.0	217	449.5	254
B. P. (°C)	−183	444.6	685	989	—

and the B.P.s. increase with atomic number from oxygen to tellurium, but drops down in polonium, which (like bismuth, the last member of Gr. VB) has an unusually low M.P.

This group of elements is rather exceptional in that, *all* the members exist in allotropic modifications (in Gr. VB, bismuth exhibits no allotropy). Ozone (O_3) and oxygen are the two allotropic modifications, both existing in the gaseous state.

Sulphur exists in several allotropic modifications. In the solid state, sulphur exists in three allotropic modifications, *viz.* α, β and γ sulphur. The α-form is the commonly occuring variety, stable upto 98°C, and belongs to the rhombic crystal system. The β-form is stable between 98° and 122°C and belongs to the monoclinic system. Both the α- and the β-forms consist of 8-membered puckered rings of sulphur and hence, are represented as S_8. However, for simplicity's sake, elemental sulphur is represented as S in chemical reactions. In the liquid state, at least two allotropes, S_λ and S_μ are recognised.

Selenium is found to exist in four allotropic modifications, three crystalline and one amorphous. The stable, commonly occuring form of selenium belongs to the hexagonal system, in which the crystals are made up of zig-zag chains of selenium atoms. Other two allotropes, α- and β-selenium, belong to the monoclinic system. The α-form and the common form of selenium are made up of Se_8 rings, analogous to the S_8 molecules. The fourth form is the amorphous selenium.

Two allotropic modifications of tellurium are known. The common and the stable form belongs to the metallic hexagonal system, in which the crystals are composed of zig-zag chains of telurium atoms, analogous to the common form of selenium. A black amorphous variety of tellurium is also known.

Polonium is reported to exist in two allotropic modifications, one belonging to the cubic and the other belonging to the rhombohedral systems of metallic crystals.

Atomic volume and atomic radius : As expected, atomic volume and atomic radius increase down the group with the increase in atomic number. This is clearly indicated in the values cited in Table 17.1.

Ionization potential : The ionization potentials of these elements decrease gradually from oxygen to polonium, with the increase in atomic number and with the consequent rise in the atomic volumes and the screening effect of the inner layer of electrons. The first ionization potential of oxygen is very high, which is primarily due to its high electronegativity compared to the other members.

Melting and boiling points : As we move down the group, the melting and the boiling points increase regularly with the atomic number. The only exception is polonium, which has a M.P. (254°C) much lower than that of tellurium (449·5°C) and nearer to that of selenium (217°C).

Metallic and non-metallic character : Along with the increase in atomic volume and decrease in ionization potential, the metallic character increases with the increase of atomic number among the members of this group. The first two members, oxygen and sulphur, are typical non-metals. Oxygen is the second most electronegative element in the periodic table and only fluorine is more electronegative than oxygen. Selenium and tellurium are weak non-metals, with tellurium exhibiting some metallic character. The heaviest member, polonium is a true metal. This gradual change from non-metallic to metallic character is less marked than what is observed in the previous Gr. VB, but it is exhibited in the following characteristics :

(a) **Change in conductivity :** Conductivity increases from the non-conductors oxygen and sulphur to seleninm and tellurium, the crystalline forms of which falls in the semiconductor class, while polonium is a conductor of both heat and electricity.

(b) **Change in the acidity of the hydrides :** All the hydrides are weak acids, yielding H^+ ions in aqueous solution. The acidity of the hydrides H_2X ($X=O, S, Se, Te$) increases with the increase in atomic number.

(c) **Nature of the oxides :** Acidity of the comparable type of oxides (say, the dioxides of the general formula RO_2) decreases from sulphur to polonium. Thus SO_2 and SeO_2 are distinctly acidic and yield H_2SO_3 and H_2SeO_3 on dissolution in water. TeO_2 is soluble in both alkalis and acids, indicating its amphoteric character, while PoO_2 is distinctly basic.

(d) **Strength of the oxyacids :** Strengths of the oxyacids (say, the 'ic' acids) decrease sharply from sulphur to tellurium. Thus, sulphuric acid, H_2SO_4, is one of the strongest protonic acids and selenic acid, H_2SeO_4, is much weaker. Telluric acid, H_6TeO_6, is even weaker. Polonium is purely metallic and does not form any oxyacid.

Electron affinity and electronegativity : Both these quantities decrease with the increase in atomic number, along with increase in atomic volume and the consequent increase in metallic character. This implies that, the heavier elements would occur in positive oxidation states in combination with the more electronegative elements (only Gr. VIIB elements, the halogens, are more electronegative).

Nature of bonding : The valence-shell electronic configuration of the Gr. VIB element is ns^2np^4, with the *ns*-orbital accommodating two paired-up electrons while, of the four *np*-electrons, two are paired-up and two are unpaired single electrons (See vol. I, p. 98.). Hence, it is clear that all of them are just two short of the 'octet' of the next inert gases. *Since they are much closer to the succeeding inert gases than the preceding ones, the question of their losing the six outermost electrons to attain the configuration of the preceding inert gases does not arise at all.* They can attain the configuration of the next inert gas in the following manner : (a) *by gaining two electrons from less electronegative elements, resulting in the formation of the di-negative chalcogenide* (X^{2-}) *ions.* However, the formation of the di-negative ions by the process, $X+2e \longrightarrow X^{2-}$, is energetically rather unfavourable, because of the *net negative electron affinity* of the chalcogens (see vol. I, Chapter II, p. 118). But, we come across many ionic oxides and sulphides (which occur in nature rather abundantly and are also easily formed from the elements), and their formation is best attributed to the favourable lattice energies (see vol. I, Chapter. III, pp. 34-36) which overcome the unfavourable electron affinities ; (b) by completing the octet by sharing the two unpaired *np*-electrons, forming two single covalent bonds and leaving two lone-pairs of electrons, one pair located in the *ns* level and the other in one *np*-level. Such molecules (like H_2O) generally act as monodentate donors towards Lewis acids and metal-ion acceptor centres ; (c) the octet can also be completed by the formation of a double bond, generating species like S=O.

Since, only the halogens (members of Gr. VIIB) are more electronegative than these elements, in most of their compounds, the chalcogens constitute the electro-negative counterpart. Electronegativity of oxygen being very high (second only to fluorine), a large number of the inorganic compounds of oxygen are predominantly ionic in character. Electronegativity of the other members of this group decrease with atomic number and are of such low value (see Table 2.8 ; vol I) that, they mostly form covalent compounds even with the most electronegative halogens. However, it must be noted here that, as the last member of this group, polonium is a true metal, its compounds are distinctly ionic in character, and more so in the lower oxidation states, obeying Fajans rules of ionic distortion.

Oxidation states : As the principal quantum number of the valence-shell of oxygen is 2, it does not possess potential *d*-orbitals for bonding purposes and hence, can form only tetra-covalent species, involving two unpaired *np*-electrons and two lone-pairs. Thus, oxygen can exhibit a valency of *two* only. But, the other elements of this group, which can utilise the *d*-orbitals for bonding purpose, exhibit valencies of 2, 4 and 6, and can form hexa-covalent species. Excepting oxygen, all the other members of Gr. VIB exhibit *formal* positive and negative oxidation states. Oxygen displays positive oxidation state only in its compound with fluorine. It is quite clear that due to their proximity to the inert gases, the negative oxidation states dominate the chemistry of the chalcogens.

Negative oxidation states : True (−2) oxidation state is achieved by oxygen and sulphur in the oxides and sulphides of more electropositive metals. In the cases of Se and Te, a *formal* (−2) state is attained in their compounds with highly electropositive elements like those of Grs. IA, IIA and also with hydrogen. The stability of the (−2) oxidation state decreases with the increase in atomic weight, and polonium exhibits practically no such negative oxidation state. This is the reason underlying the increase in the reducing character of the hydrides (XH_2) from sulphur to polonium.

Positive oxidation states : The valence-shell electronic configuration of ns^2np^4 suggests the existence of formal oxidation states of (+4) and (+6), corresponding to the involvement of the four *np*-electrons and all the six *np*-and *ns*-electrons in bonding with more electro-negative elements. As already pointed out, oxygen displays the (+2) oxidation state with fluorine in F_2O.

Sulphur and the other heavier members have vacant *'d'*-orbitals in their outermost shell. In the normal or ground state, all these elements have two unpaired *np*-electrons, which can form only two single covalent bonds. On excitation, one of the paired-up electrons in the *np*-level gets unpaired and is promoted to one of the vacant *nd*-levels, resulting in a valence-shell configuration of ns^2np^3nd. This results in making four unpaired electrons available for the formation of four single covalent bonds in the formal (+4) oxidation state. On further excitation, the two paired-up *ns*-electrons are also unpaired and one is promoted to one of the vacant *nd*-orbitals, resulting in the generation of the formal (+6) oxidation state by attaining the valence-shell configuration of $ns^1np^3nd^2$, and thus making provisions for the formation of six electron-pair bonds. However, it must be kept in mind that, in these excited states, the atoms undergo suitable hybridisation process, resulting in the energetically stable geometrical arrangements of the electron-pairs (both bond-pairs and lone-pairs) in the resultant molecules.

The positive and negative oxidation states, displayed by the members of Gr. VIB, are given in the following table, along with some suitable examples :

TABLE 17.2

(Oxidation states of the Gr. VIB elements)

Oxidation state	Oxygen	Sulphur	Selenium	Tellurium	Polonium
+6	—	SO_3 H_2SO_4	SeO_3 H_2SeO_4	TeO_3 H_6TeO_6	—
+4	—	SO_2 H_2SO_3	SeO_2 H_2SeO_3	TeO_2	—
		SCl_4	$SeCl_4$	$TeCl_4$	—
−1	—	Na_2S_2	—	—	—
−2	H_2O Na_2O	H_2S Na_2S	H_2Se	H_2Te	—

Catenation or self-linkage : Like the first two members of the previous group of elements (N and P of Gr. VB), oxygen and sulphur exhibit the property of catenation or self-linkage to a limited extent. Thus, three oxygens are linked together in the ozone molecule, O_3. Sulphur exhibits this property to a greater extent, eight sulphur atoms being linked up in the S_8-molecule. The stable varieties of selenium and tellurium also contains several atoms linked together in the form of zig-zag chains. However, it must be kept in mind that the O—O, S—S, Se—Se, Te—Te bonds are very weak in comparison with the similar bonds of the Gr. VB (N—N and P—P bonds) and Gr IVB (C—C and Si—Si) elements.

Electron donor properties : As discussed previously, in the molecules like H_2O, R_2O, R_2S, etc., two lone-pairs of electrons are located on oxygen and sulphur, as a result of which, they can act as electron donors. Such donor capacity decreases with the increase in atomic number. Thus, many bi-covalent oxygen and sulphur compounds are good donors, while the corresponding selenium and tellurium compounds have practically no donor property. This is quite understanable, because the electronegativity of these elements decrease with atomic number.

Chemical reactivity : Chemical reactivity in this group of elements decreases from oxygen to tellurium. Oxygen exhibits high activity towards the most electropositive alkali (Gr. IA) and the alkaline earth (Gr. IIA) metals, even under ordinary conditions. But, sulphur reacts with them only at high temperatures, while selenium and tellurium show much less tendency to form selenides and tellurides. With the other less electropositive elements, oxygen and sulphur combine at elevated temperatures, but selenium and tellurium show less activity. This is reflected in the progressively lower heats of formation of the oxides, sulphides, selenides and tellurides. In their combination with more electronegative elements of the Gr. VIIB (the halogens), the same trend is displayed by sulphur, selenium and tellurium.

Hydrides ; All the elements of Gr. VIB form hydrides of the general formula H_2X, where $X=O, S, Se, Te$ and Po. Apart from water (which is a liquid), H_2S, H_2Se and H_2Te are foul-smelling gases at ordinary temperature. Water is a liquid and has much higher melting and boiling points due to the association of its molecules through hydrogen bonding (See vol. I., chapter IX, p. 335). Boiling points of H_2S, H_2Se and H_2Te gradually decrease in that order. Variation of some other important properties of these hydrides may be represented as :

Ionic character.
Acidity.

$\xrightarrow{\text{increases}}$

H_2O, H_2S, H_2Se, H_2Te

$\xleftarrow{\text{increases}}$

Thermal stability.
Covalent character.
Hydrogen bonding.

All the hydrides are weak protonic acids. The acidity of the hydrides is found to increase from H_2O to H_2Te. This is rather unexpected, as the electronegativity decreases in that direction. However, the increase in atomic volume with atomic number must also be taken into consideration, as the sum of the covalent radii of hydrogen and the chalcogen determines the H—X bond distance. A large H—X distance will definitely fecilitate the release of proton and hence, will increase the acidity of the hydride. This increase in acidity due to the increase in atomic volume of the chalcogens with atomic number, overcomes the opposite effect due to the decrease in electronegativity down the group.

In all these hydrides, the element displays its formal (−2) oxidation state, as hydrogen is more electropositive than any of them. But, all these hydrides are predominantly covalent, with ionic character increasing from H_2O to H_2Te due to the same reason which results in the increase of acidity in that direction.

The reducing character of these hydrides decreases down the group, which may be attributed to the increase in their acidity and the consequent release of hydrogen as H^+ and not as H^- or H-atom.

Hydrogen bonding capacity is maximum in H_2O (See vol. I, chapter IX), and is responsible for its exceptional properties like high B.P., dielectric constant etc. Along with the decrease in electronegativity from oxygen to polonium, the hydrogen bonding character decreases, and becomes negligible, for all practical purposes, after sulphur.

H_2O_2 (see vol. I, chapter IX) and H_2S_2 are two other hydrides known. H_2O_2 is much more stable than H_2S_2, which decomposes at ordinary temperatures to H_2S and S. H_2S_2 is not at all an oxidising agent like H_2O_2. The structure of H_2S_2 is similar to that of H_2O_2.

Halides : The names of the different halides formed by the Gr. VIB elements are given in the following table :

TABLE 17.3

Element	Fluorides	Chlorides	Bromides	Iodides
Oxygen	F_2O, F_2O_2	—	—	—
Sulphur	S_2F_2, SF_4, SF_6	S_2Cl_2, SCl_2, SCl_4	S_2Br_2	—
Selenium	Se_2F_2, SeF_4, SeF_6	Se_2Cl_2, $SeCl_4$	$SeBr_2$, $SeBr_4$	—
Tellurium	TeF_4, TeF_6	$TeCl_2$, $TeCl_4$	$TeBr_2$, $TeBr_4$	TeI_4
Polonium	—	$PoCl_2$, $PoCl_4$	$PoBr_2$, $PoBr_4$	PoI_4

True halides of oxygen are restricted to the two fluorides, F_2O and F_2O_2, as all the other halogens are less electronegative than oxygen and hence, binary compounds of oxygen with Cl_2, Br_2 and I_2, should better be considered as oxides of halogens, rather than halides of oxygen.

Monohalides : Monohalides of the general formula A_2X_2 (X=F, Cl and Br), are known for S, Se and Te. S, Se and Te form the monochlorides, and monobromides are formed by S and Se. Sulphur yields S_2F_2 in addition. Of these, the sulphur monochloride is of some importance and it is a planar molecule with the sulphur in the sp^3-state of hybridisation.

All these monohalides are hydrolysed slowly by water: $2S_2X_2+2H_2O=4HX+SO_2+3S$. The ease of hydrolysis decreases from sulphur to tellurium.

Dihalides : Difluorides of the chalcogens are not known. Dichlorides are formed by S, Se, Te and Po, while dibromides are known for S, Se Te and Po. Sulphur dichloride, SCl_2, spontaneously decomposes to the monohalide and chlorine. All the dihalides are hydrolysed by water. The dihalides undergo disproportionation on heating : $2SeCl_2 \rightarrow SeCl_4+Se$. The ease of disproportionation decreases with the increase in atomic number.

Tetrahalides : Tetrafluorides of S, Se and Te are known. SF_4 is a gas, SeF_4 is liquid and TeF_4 is a solid. Tetrachlorides of S, Se, Te and Po are also known. SCl_4 is an unstable liquid. $SeBr_4$, $TeBr_4$ and $PoBr_4$ are all solids. But, only Te and Po form tetraiodides. The tetrafluorides have trigonal bipyramidal structure, involving sp^3d-hybridisation (see vol. I, p. 150 and 156), with the four halides occupying four corners and the lone-pair sitting in the fifth position. It is due to the presence of this lone-pair that the tetrahalides can act as monodentate donors (Lewis bases) towards acceptor centres, to which they donate the lone-pair of electrons. The tetrahalides are more reactive than the corresponding hexahalides.

Hexahalides : Excepting polonium, S, Se and Te form hexafluorides. All these hexafluorides are colourless gases and covalent in character. Hexachlorides and hexabromides of these elements are not known. The hexafluorides have octahedral structures, involving sp^3d^2-hybridisation (see vol. I, p. 150 and 157). The stability of the hexahalides decreases from sulphur to tellurium. Thus, SF_6 is very stable and inert, and is not hydrolysed by water. SeF_6 is slowly hydrolysed and TeF_6 is completely hydrolysed in 20-24 hours. Since all the three atoms (S, Se, Te) possess vacant '*d*'-orbitals usable for the initiation of nucleophilic attack by H_2O, the factor responsible for the observed difference in hydrolytic stability is probably the increase in size of the central element, resulting in less efficient shielding by the six fluorine atoms. It is due to this, the central element becomes more exposed to attack by H_2O and other nucleophilic reagents. The increase in ionic nature of the chalcogen-halogen bond (S—Cl, Se—Cl etc.) may also contribute towards the decrease in hydrolytic stability from SF_6 to TeF_6.

Oxides : Oxides of this group are the binary compounds of oxygen with the other chalcogens. The well-known oxides of the chalcogens are :

SO		TeO	PoO
SO_2	SeO_2	TeO_2	PoO_2
SO_3	SeO_3	TeO_3	

Monoxides : SO is a very unstable acidic oxide, and forms dithionous acid ($H_2S_2O_4$) on reacting with water. TeO is also unstable and basic, and dissolves in H_2SO_4, giving a red solution. PoO is definitely basic and dissolves in mineral acids, yielding bivalent polonium salts.

Dioxides : All of S, Se, Te and Po yield the dioxides of the formula XO_2, of which SO_2 and SeO_2 are distinctly acidic in character and yield sulphurous acid (H_2SO_3) and selenous acid (H_2SeO_3) on dissolution in water. But, TeO_2 is rather amphoteric and dissolves in alkalis to yield tellurites (*e.g.* Na_2TeO_3), and also in acids to yield basic salts. PoO_2 is distinctly basic. SO_2 is a gas, but SeO_2 is a solid comprising of infinite chains of the formula $(SeO_2)_n$. TeO_2 and PoO_2 are ionic solids. SO_2 has a planar triangular structure, involving sp^2-hybridisation, with two corners occupied by the two oxygens and the third by a lone-pair. This is the reason of SO_2 being capable of acting as a Lewis base.

Trioxides : SO_3, SeO_3 and TeO_3 are the three known trioxides. All of them are distinctly acidic in nature and form the '*ic*' acids on dissolution in water :

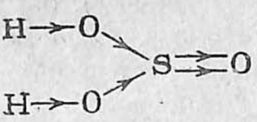
$$SO_3+H_2O = H_2SO_4 ;$$
$$SeO_3+H_2O = H_2SeO_4 ;$$
$$TeO_3+3H_2O = H_6TeO_6.$$

The acidic character of the trioxides decreases from sulphur to tellurium, paralleling the decrease in electronegativity in that direction.

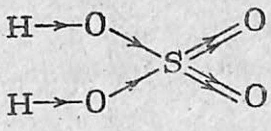
The SO_3 molecule possesses plane triangular structure, involving sp^2-hybridisation (see vol. I, chapter III, p. 155). The other trioxides probably have similar structures in the gaseous state.

Because of the availability the outer '*d*'-orbitals, SO_3 can act as a Lewis acid and as an oxidising agent, by accommodating electrons from other reacting substrates.

Oxyacids : Of S, Se, and Te, sulphur forms a large number of oxyacids. The comparable oxyacids of these three elements, (the '*ous*' acids and the '*ic*' acids), are obtained by the dissolution of the dioxides and the trioxides respectively in water. Just like the oxides, the acid-strengths of both the 'ous' acids and the 'ic' acids decrease from sulphur to tellurium, i.e. $H_2SO_3 > H_2SeO_3 > H_2TeO_3$ and $H_2SO_4 > H_2SeO_4 > H_6TeO_6$. Also, the 'ic' acids are much stronger than the corresponding 'ous' acids, i.e., $H_2SO_4 > H_2SO_3$; $H_2SeO_4 > H_2SeO_3$ etc. This is quite logical because, an increase in the number of oxygen atoms attached to the central chalcogen atom (in the molecule of the oxyacid) increases the electron-attracting power of the chalcogen atom. Thus, the effective electronegativity of sulphur in SO_3 is greater than that of sulphur in SO_2. Now, the simple bond structures of H_2SO_3 and H_2SO_4 are :



(H_2SO_3)



(H_2SO_4)

Since, the electron-attracting power of the sulphur atom in sulphuric acid is greater, it will exert this effect to the bond-pair holding the H—O bonds through the hydroxyl oxygen atom and pull this bond-pair towards itself. This inductive effect (see vol. I. p. 165), shown in the above figure, will result in a more facile release of protons in the case of H_2SO_4, compared to that of H_2SO_3 which contains lesser number of oxygen atoms attached to the central sulphur atom.

OXYGEN

It has been mentioned earlier that oxygen is the most abundant element and in the free state, it constitutes about 21% of our atmosphere. It is absolutely essential for the respiration of the human beings and other higher forms of life. Its isotopic composition is :

${}_8O^{16}$	${}_8O^{17}$	${}_8O^{18}$
99.7%	0.1%	0.2%

It occurs in two allotropic forms, O_2 (oxygen) and O_3 (ozone).

Special characteristics of oxygen :

Following the general principle of the periodic classification of elements, oxygen, the first member of Gr. VIB, exhibits considerable difference in properties from the higher members. Such differences are due to the following reasons :

(i) Small size and high electronegativity of oxygen : Because of this, the compounds of oxygen with other elements are primarily ionic, in most of which it is present as the di-negative O^{2-} ion. But, the occurrence of true S^{2-}, Se^{2-} and Te^{2-} are far less common.

(ii) As its valency shell has $n=2$, it has no '*d*'-orbitals utilisable for bond formation by the octet expansion. As a result, its maximum covalency is 2. But, the higher members can expand their octet due to the availability of outer '*d*'-orbitals and can exhibit covalencies of both 4 and 6. This also is the reason of the diatomic nature of oxygen.

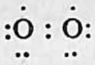
(iii) Except with fluorine, oxygen does not exhibit positive oxidation state. The reason for this lies in the very high electronegativity of oxygen, which is second only to fluorine. But, for the other members, the positive oxidation states are more common.

(iv) Due to the presence of two unpaired electrons, the oxygen molecule is strongly paramagnetic, while all the other members are diamagnetic in character.

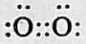
(v) Due to its high electronegativity and small size, oxygen compounds participate strongly in hydrogen bonding with compounds containing hydrogen.

(vi) Due to its high dissociation energy, large activation energies are essential to initiate oxidation reactions by molecular oxygen. This is the reason for the relative lack of activity of oxygen at ordinary temperatures. However, most of these reactions are highly exothermic and once started, goes on with vigour. This is the reason of its high activity at elevated temperatures.

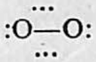
Structure of the O_2-molecule. Any structure of the oxygen molecule must explain (i) its paramagnetic behaviour and (ii) its high dissociation energy (~118 Kcals/mole). The structures I and II were first proposed for the O_2 molecule :


$:\underset{\cdot\cdot}{\dot{O}}:\underset{\cdot\cdot}{\dot{O}}:$

I


$:\ddot{O}::\ddot{O}:$

II


$:O\overset{\cdots}{\underset{\cdots}{-}}O:$

III

The structure I accounts for the paramagnetism of the O_2-molecule, but fails to explain its high dissociation energy, since, only a single bond holds the two oxygen atoms together. Also, it does not conform to the octet rule. The structure II, because of the presence of a double bond in it, can account for the high dissociation energy of the O_2-molecule ; but, the lack of the presence of unpaired electrons cannot explain its paramagnetic behaviour. Linus Pauling has suggested the structure III, in which the two oxygen atoms are held together by two three-electron bonds and one normal electron-pair covalent bond. Each of the two three-electron bonds has one unpaired electron, accounting for the parmagnetism. The two three-electron bonds (each of about half the strength of a normal electron-pair covalent bond) and one normal electron-pair bond, together impart the same strength of bonding as that of a double bond. Hence, it can account for the high dissociation energy of the O_2-molecule. However, it must be noted that the existence of two unpaired electrons, giving rise to its paramagnetism and its high dissociation energy, is best explained by the application of the *molecular orbital theory* (M. O. Theory)

For all practical purposes, oxygen is mostly obtained by the fractional evaporation of liquid air, and to some extent, as a by-product of electrolytic manufacture of hydrogen, caustic soda etc. The other methods of preparation of oxygen from compounds of oxygen are of little practical use. Hence, only the principles of a few such methods are mentioned here.

1. **By the thermal decomposition of salts of some oxyacids :** Salts of oxyacids (rich in oxygen), like the nitrates and chlorates, decompose on heating to a high temperature, yielding oxygen. The

presence of a catalyst often lowers the decomposition temperature to a considerable extent.

$$2NaNO_3 \xrightarrow{\text{Red heat}} 2NaNO_2+O_2\ ;$$
$$2KClO_3 \xrightarrow{400^\circ C} 2KCl+3O_2\ ;$$
$$2KClO_3 \xrightarrow[\text{(Catalyst)}]{MnO_2} 2KCl+3O_2\ ;$$

The last reaction is utilised for the preparation of oxygen in the laboratory.

2. By the thermal decomposition of oxides and peroxides.

$$2HgO \rightarrow 2Hg+O_2\ ;$$
$$2BaO_2 \rightarrow 2BaO+O_2.$$

Oxygen from air : Atmospheric air is first passed through several purifiers and then liquefied. The liquid air is then subjected to fractional evaporation. At first, the more volatile nitrogen (b.p. 77.3° K) boils off readily and oxygen, being less volatile (b.p. 90.04°K), comes off afterwards (for details see volume I, pp. 314-316).

Oxygen by the electrolysis of water : This process is adopted for the manufacture of hydrogen, and oxygen is obtained as a by-product. The details of this process is given in volume I pp. 326-327.

Physical properties : Oxygen is a colourless, odourless and tasteless gas, slightly soluble in water. It can be liquefied by pressure, only after cooling below its critical temperature. Liquid oxygen is pale blue in colour, boiling at -183°C and freezing at -219°C. Gaseous, liquid and solid oxygen are all paramagnetic.

Chemical properties : Oxygen combines directly with almost all elements except the inert gases, and forms stable compounds called *oxides*. Oxygen is a vigorous supporter of combustion, but itself is non-combustible.

Inspite of its chemical affinity towards most of the elements, oxygen, at ordinary temperatures, is comparatively inert. This is due to its high dissociation energy of 118 Kcals/mole, requiring a considerable activation energy which can be attained only at comparatively high temperatures. But, most of such reactions are strongly exothermic, and once initiated, proceed spontaneously.

1. Formation of oxides by direct combination.

Excepting some noble metals like gold and platinum, oxygen reacts with most of the metals and non-metals at elevated temperatures, forming different types of oxides. Some typical reactions of oxygen with metal and non-metals are :

$$\begin{aligned} 2H_2+O_2 &= 2H_2O\ ; & 4Na+O_2 &= 2Na_2O\ ; \\ 2Ca+O_2 &= 2CaO\ ; & 4Al+3O_2 &= 2Al_2O_3\ ; \\ C+O_2 &= CO_2\ ; & 4P+5O_2 &= P_4O_{10}\ ; \end{aligned}$$

$$S+O_2=SO_2.$$

2. Oxidation reactions.

Oxygen effects oxidation of many inorganic compounds at elevated temperatures in presence or absence of catalysts.

$$4NH_3+5O_2 \underset{}{\overset{\text{Pt-gauge}}{\rightleftharpoons}} 4NO+6H_2O\ ;$$

$$2SO_2+O_2 \overset{V_2O\ /\text{Pt-asbestos}}{\rightleftharpoons} 2SO_3\ ;$$

$$2NO+O_2 \rightleftharpoons 2NO_2.$$

3. Combustion of organic compounds in oxygen.

At or near the ignition temperatures, oxygen reacts with many organic compounds. When it is present in excess, the ultimate products are mainly carbon dioxide and water :

$$CH_4+2O_2=CO_2+2H_2O\ ;$$

$$2C_2H_2+3O_2=4CO_2+2H_2O\ ;$$

$$2C_6H_6+15O_2=12CO_2+6H_2O\ ;$$

$$C_{12}H_{22}O_{11}+12O_2=12CO_2+11H_2O.$$

4. Formation of ozone.

On passing silent electric discharge through oxygen, ozone is formed : $3O_2 \rightleftharpoons 2O_3$.

Atomic Oxygen : Because of its high dissociation energy, it requires a very high temperature to generate atomic oxygen from molecular oxygen :

$$O_2 \xrightarrow{\text{heat}} 2[O]\ ;\ \triangle H=+116\ \text{Kcals.}$$

The reaction, being highly endothermic, requires the continuous presence of high temperature.

On passing electric discharge through gaseous oxygen at low pressure, 20% of the oxygen molecules dissociate, yielding atomic oxygen.

Atomic oxygen is much more reactive than molecular oxygen at ordinary temperatures. It reacts with chlorine to produce Cl_2O and ClO_2, and forms BrO_2 with bromine. It reacts vigorously with several organic compounds like methane, ethylene, benzene and the aliphatic alcohols.

The presence of atomic oxygen is detected by the greenish-white luminescence produced, when atomic oxygen reacts with nitric oxide.

Oxides : Oxides are the binary compounds of oxygen with less electronegative elements, in which oxygen constitutes the negative counterpart, occuring in the (−2) oxidation state. This covers all elements except fluorine, which is more electronegative than oxygen.

Formation of the oxide ion (O^{2-}) from molecular oxygen takes place through two steps, each involving considerable amount of energy :

$$\tfrac{1}{2}O_2(g) \rightarrow O(g) \, ; \qquad \Delta H = 60 \text{ Kcal/mole} \, ;$$
$$O(g) + 2e \rightarrow O^{2-}(g) \, ; \qquad \Delta H = 176 \text{ Kcal/mole.}$$
$$\text{or, } \tfrac{1}{2}O_2(g) + 2e \rightarrow O^{2-}(g) \qquad \Delta H = 236 \text{ Kcals/mole.}$$

Thus, the process of oxide-ion formation from molecular oxygen requires a large amount of energy and hence, oxide formation is energetically rather unfavourable. But, we know that many ionic oxides (involving the O^{2-} ion) exist, and this is because of the very high lattice-energy of such oxides, which more than compensates the high energy required for the formation of the O^{2-} species. In some cases, the lattice-energy is not sufficiently high to effect complete electron-transfer from the metal atoms to the oxygen, and in those cases, the M—O bonds exhibit covalent character.

Classification of oxides : Several different ways of classifying oxides have been adopted by different authors. Of these, (i) the classification based on the reactions of the oxides with water and (ii) the method based on their over-all structures, are most useful.

(i) *Classification of oxides based on their reactions with water :* In this classification, an oxide is termed as a basic (ionic) oxide, whose aqueous solution reacts basic (i.e. pH>7). If such a basic oxide is represented as MO, it will react with water as :

$2MO+H_2O = 2MOH \rightleftharpoons 2M^+ + 2OH^-$, i.e., it will generate OH^- ions, or displace OH^- ions from water, making it basic or alkaline. Since, such basic oxides are ionic, containing the O^{2-} ion, its basic character in water may also be explained by the reaction :

$$O^{2-} + \underset{\text{(from water)}}{H^+—OH^-} \rightarrow 2OH^-$$

Thus, we can visualise the oxide ion, O^{2-}, as the *basic anhydride*. It is also clear from the above reaction that, such bases will react with acids like HCl and neutralise it :

$$CaO(s)+2HCl(aq) \rightarrow Ca^{+2}(aq)+2Cl^-(aq)+H_2O.$$

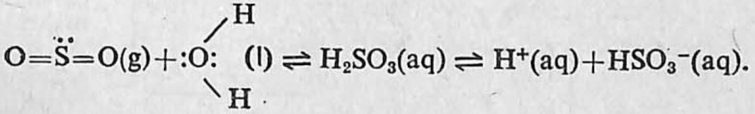
In a similar manner, the basic character of the peroxides and the superoxides can also be explained :

$$\underset{\text{peroxide}}{O_2^{2-}} + H^+—OH^- \rightarrow O_2H^- + OH^- \,;$$

$$\underset{\text{superoxide}}{2O_2^-} + H^+—OH^- \rightarrow O_2 + O_2H^- + OH^-.$$

In all the above reactions, the O^{2-} ion behaves as a Lew s base and water as Lewis acid.

Acidic (covalent) oxides are those oxides, whose aqueous solutions are acidic ($pH<7$). These are generally oxides of non-metals. Taking the example of sulphur dioxide, their acidic behaviour in aqueous solution can be explained as :



$$O=\ddot{S}=O(g) + :\!\overset{H}{\underset{H}{O}}\!: (l) \rightleftharpoons H_2SO_3(aq) \rightleftharpoons H^+(aq)+HSO_3^-(aq).$$

Thus, such oxides may be considered as *acid anhydrides*. Metallic oxides like Mn_2O_7, in which the metal is in a high oxidation state, react with water to form acids :

$$Mn_2O_7(s)+H_2O(l) \rightarrow 2HMnO_4(aq) \rightleftharpoons 2H^+(aq)+2MnO_4^-(aq)$$

Both the above reactions are acid-base reactions in which the oxides act as Lewis acids and water acts as Lewis base. CrO_3 also reacts similarly :

$$CrO_3(s)+H_2O(l) \rightarrow H_2CrO_4(aq) \rightleftharpoons H^+(aq)+HCrO_4^-(aq).$$

Amphoteric oxides : The amphoteric oxides have the capacity of reacting with both acids and bases. The reactions of zinc oxide will represent such a model :

$ZnO(s)+2HCl(aq)=Zn^{+2}(aq)+2Cl^{-}(aq)+H_2O$;
$ZnO(s)+4OH^{-}(aq)=Zn(OH)_4^{2-}(aq)$ or, $(ZnO_2^{2-}+2H_2O.)$

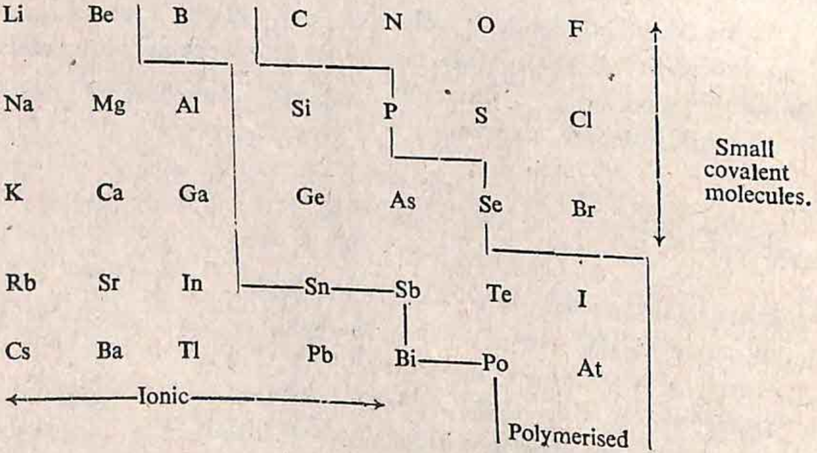
Netrual Oxides : These oxides are considered as neutral in the sense that, they have no apparent reaction with water, acids or bases under normal conditions. Examples of such oxides are N_2O, NO and CO.

It must, however, be kept in mind that this classification is applicable to the representative elements only.

Variation of the chemical properties of the oxides of the representative elements, from left to right in a period and down a particular group, has been discussed in volume I, chapter **II**, pp. 128-129.

Classification of oxides based on their over-all structures : In this method, the oxides are classified as ionic, covalent and polymeric covalent. The following table marks the elements (representative) forming each class of the oxides :

TABLE 17·4.



It is to be noted here that the ionic oxides of this classification are the basic oxides, while the covalent oxides are the acidic oxides of the previous method of classification.

Uses of Oxygen : The real importance of oxygen is because of its vital role in processes like respiration and combustion. It is used for helping the respiration of weak persons, for the respiration of under-water divers (mixed with nitrogen or carbon dioxide), to help the respiration of mountaineers and workers working at high altitudes.

In industry, it is used in the oxy-hydrogen and oxy-acetylene flames for welding and cutting processes.

Liquid oxygen, mixed with suitable liquid fuels, is used in the propulsion of jets and rockets. Liquid oxygen is also used for the production of low temperatures in the laboratory.

OZONE

Ozone (O_3) is the only allotropic modification of oxygen. It is a highly unstable gas which occurs in traces in the upper atmosphere.

Preparation : Ozone (or rather ozonized oxygen) is usually prepared by the passage of *silent electric discharge* through oxygen. The mechanism of formation of ozone from oxygen involves the partial dissociation of some oxygen molecules to atomic oxygen in the first step. In the second step, the O_3 molecule is formed by collisions between atomic oxygen and oxygen molecules :

$$O_2 \rightarrow O+O,$$
$$O+O_2 \rightarrow O_3\ ;\ \triangle H=-241\text{Kcals}.$$

These O_3 molecules are in a highly energised state and get themselves stabilised by transferring its excess energy to the remaining oxygen molecules by collisions.

The maximum concentration of ozone achieved in this method is 10%.

Ozone is also formed when oxygen is irradiated with ultra-violet light of wavelengths 1750Å to 2500Å. Some of the oxygen molecules are activated by absorbing uv radiation in the first step. In the second step, an activated O_2^* molecule and a normal O_2 molecule undergo collision to form ozone and atomic oxygen.

$$O_2 \xrightarrow{h\nu} O_2^*\ \text{(activated oxygen molecule)}\ ;$$
$$O_2^*+O_2 \longrightarrow O_3+O.$$

The presence of O_3 in the upper atmosphere is probably due to this reaction.

In a more recent method, ozone is obtained in higher yields by electrolysing a concentrated solution of perchloric acid at a very low temperature (−50°C), using a lead cathode and platinum anode. The mechanism of formation of ozone in this method is not known with certainty, but it is believed that ozone is produced by secondary reactions between the products generated by the anodic oxidation of water.

For the isolation of ozone, ozonised oxygen is liquefied first, when the liquid separates into two layers. The upper layer (deep blue) is a solution of ozone in liquid oxygen and the lower layer (violet), is a solution of oxygen in liquid ozone. This lower layer is subjected to fractional distillation, when pure liquid ozone is obtained.

Ozone is a blue gas with bad fishy odour. Its vapour density corresponds to the molecular formula O_3. On cooling (by liquid oxygen or nitrogen), it is converted into a blue liquid (b.p. −112.4°C), diamagnetic in character. The critical temperature and pressure for ozone is −5°C and 92·8 atmospheres respectively. It is more soluble in water than molecular oxygen (~ 0·5 vols. in 1 vol. of water) and is also soluble in CCl_4 and $CHCl_3$.

Ozone is one of the most powerful oxidising agents, which is apparent from the E°-values of the following systems :

A : $O_3+2H^++2e \rightleftharpoons O_2+H_2O$; $E^\circ=+2{\cdot}07$ volts ;

B : $O_3+H_2O+2e \rightleftharpoons O_2+2OH^-$; $E^\circ=+1{\cdot}24$ volts.

The couple (A) clearly indicates that ozone is one of the most powerful oxidising agents in acid solution, exceeded only by fluorine, oxygen difluoride, atomic oxygen and the hydroxyl radical. The couple (B) shows that, it is a less powerful oxidising agent in alkaline medium. But, even in alkaline medium, its oxidising power is less than only the hydroxyl radical.

It oxidises (i) lead sulphide to lead sulphate, moist sulphur to sulphuric acid, iodide to iodine, the ferrous salts to the ferric salts, nitrite to nitrate and moist iodine to iodic acid :

(i) $PbS+4O_3=PbSO_4+4O_2\uparrow$;

(ii) $S+H_2O+3O_3=H_2SO_4+3O_2\uparrow$;

(iii) $2I^-+H_2O+O_3=I_2+2OH^-+O_2\uparrow$;

(iv) $Fe^{+2}+2H^{+}+O_3=Fe^{+3}+H_2O+O_2\uparrow$;

(v) $NO_2^{-}+O_3=NO_3^{-}+O_2\uparrow$;

(vi) $I_2+H_2O+5O_3=2HIO_3+5O_2\uparrow$

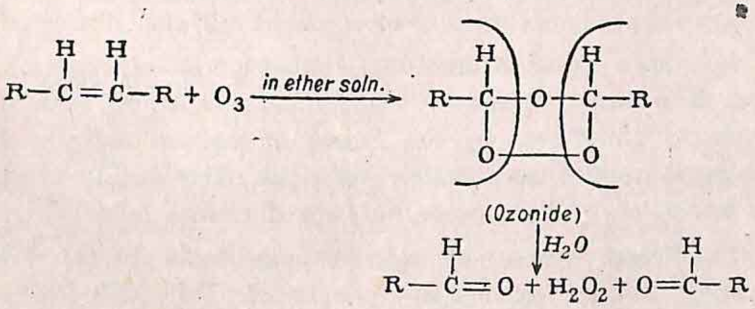
It is clear from the above reactions that only one oxygen atom per ozone molecule is utilised for effecting oxidation. However, below 40°C, all the three oxygen atoms are utilised in oxidising sulphur dioxide to sulphur trioxide :

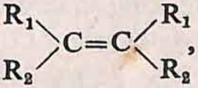
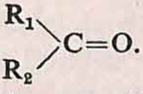
$$3SO_2+O_3=3SO_3.$$

On reacting with solid potassium and cesium hydroxide, ozone yields brown solid products of uncertain nature, possessing oxidising powers like peroxides.

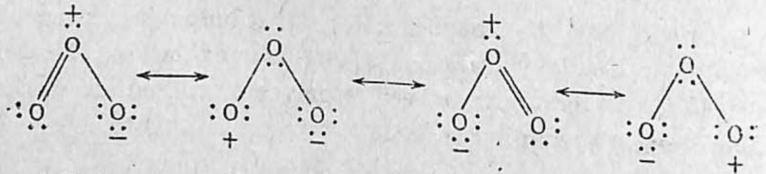
Ozone is metastable under all conditions and is reverted to molecular oxygen with the evolution of heat : $O_3 \rightleftharpoons \frac{3}{2}O_2$, $\Delta H = -34.2$. Kcals. This exothermic reversion is catalysed by various substances like, Ag, Pt, CuO, MnO_2 etc.

Addition of ozone to carbon-carbon multiple bonds (double and triple bonds. See vol. I, chapter III, pp. 158–160) is of much importance in organic chemistry in determining the position of the double bonds. The ozonides formed yield aldehydes or ketones on hydrolysis by the rupture of the double bond present :



If the starting olefin is of the type  , the products are two molecules of ketones,  .

Structure of Ozone : The electron diffraction study of ozone in the gaseous state, along with the infra red data, indicates that, the three oxygen atoms in ozone are at the three corners of an isosceles triangle with an angle of 127 ± 3° and an O—O bond distance of 1.26 ± 0.02 Å, which is intermediate between an O—O single bond (1.48Å) and an oxygen-oxygen double bond (1.10Å), and thus



essentially involves more than one resonating forms, each making nearly equal contribution to the over-all resonance hybrid.

SULPHUR

Occurrence : As already mentioned, sulphur is one of the fairly abundant elements, occurring widely in the earth's crust. It occurs in the free state as well as in the combined form, as sulphides and sulphates. In the native state, it is found in the volcanic regions of Sicily of Europe, Lousiana and Texas of U.S.A. and Mexico. In the combined state, it occurs widely as sulphide ores like galena (PbS), cinnabar (HgS), copper pyrites ($CuFeS_2$), iron pyrites (FeS_2) and zinc blende (ZnS) and as sulphates like gypsum ($CaSO_4.2H_2O$), Epsom salt ($MgSO_4.7H_2O$), celestine ($SrSO_4$) etc. Sulphur is also an essential constituent of a large number of substances of animal and plant origin like eggs, various proteins, hair, garlic, mustard etc.

Isolation : Most of the global production of sulphur is obtained from the deposits at Sicily by the *Sicilian process* and from those at Louisiana and Texas by the *Frasch process*. Since the Frasch process is applied more widely and yields purer quality of sulphur, the principles of this process only are discussed here.

The Frasch process of isolation of sulphur : In the American deposits, sulphur occurs at a depth of 700 – 1500 feet. Three concentric pipes are sunk down into the sulphur bed (Fig. 17.5) and superheated water (at ~ 180°C) is poured through the outermost tube. This superheated water melts the sulphur (m.p. 112.8°C). Now, hot compressed air is passed through the central tube, when the simultaneous upward thrust of the compressed hot air and the superheated water forces the molten sulphur (as a foam of water, sulphur and air) up the pipe at the middle, which is collected in suitable vessels. On cooling, the sulphur solidifies and is taken off from the water. The process is continuous and the purity of sulphur, thus obtained, is in the region of 99.5%. It can be further purified by distillation.

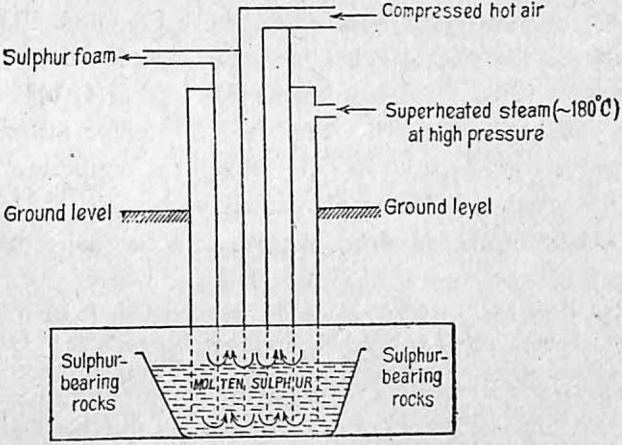


Fig. 17·5

Allotropy of sulphur : Elemental sulphur exists in several allotropic modifications. In the solid state it occurs in three well-defined forms, α, β and γ. The common variety of sulphur, the α-form, is crystalline, bright yellow in colour and belongs to the *orthorhombic system* [See vol. II. Appendix (The Solid State)]. It is insoluble in water but soluble in carbon disulphide. On heating above 95.5°C, it is slowly converted into the monoclinic β-sulphur, which is dull-yellow in colour and soluble in CS_2, but not in water. Both the rhombic (α) and the monoclinic (β) forms possess puckered S_8-rings [Fig. 17·6 (a)] as the structural units, which has been confirmed by the determination of their molecular weights by cryoscopic methods in carbon disulphide solvent. The S—S bond lengths are 2.12 Å and the S—S—S angles are 105.4°.

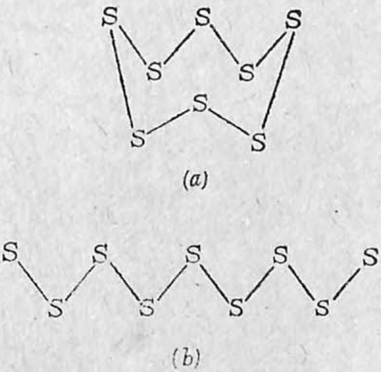


Fig. 17·6

When solid sulphur is heated above its melting point (112.8°C), the liquid sulphur retains its S_8-ring structure; but, as the temperature reaches ~ 160°C, the rings are ruptured due to the *homolytic fission* of some of the S-S bonds (See vol. I., Ch. III, p. 162-163), generating *free-radicals* at both the ends. These species are highly reactive and attack other such chains and rings, forming long zig-zag chains of sulphur atoms [see Fig. 17·6 (b)]. The liquid becomes more viscous with the rise of temperature, attaining maximum viscosity around 200°C. When the temperature is further raised, the viscosity decreases, probably because the long chains break up, and liquid sulphur behaves as a normal liquid up to its boiling point.

When liquid sulphur is suddenly chilled by pouring into ice-cold water, *plastic sulphur* is obtained. This is a rubber-like material, insoluble in CS_2, possessing a fibrous structure containing zig-zag chains of sulphur, and is also known as ν-sulphur.

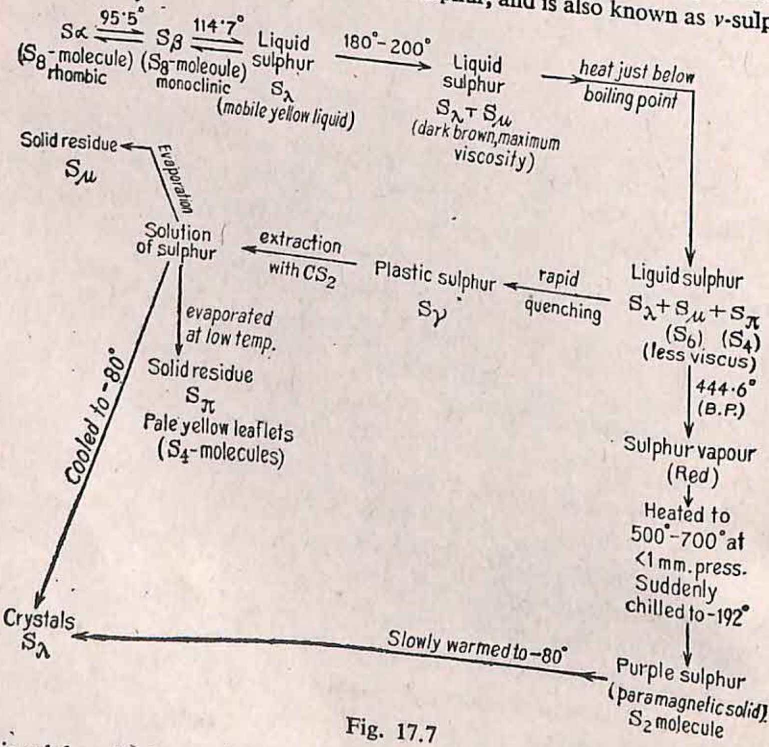


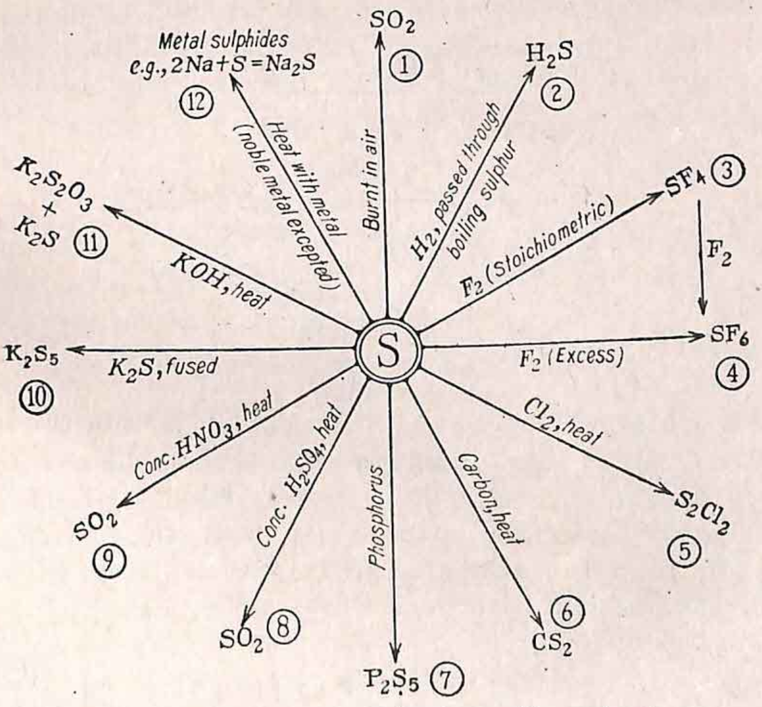
Fig. 17.7

Plastic sulphur slowly reverts to the rhombic (α) variety or the monoclinic form, depending on the temperature at which it is kept. On being extracted with CS_2, freshly prepared plastic sulphur leaves an insoluble residue, which is probably amorphous and is known as the μ-sulphur. On cooling the CS$_2$ extract to -80°C, rhombic sulphur crystallises out. When the filtrate from this operation is slowly evaporated at a low temperature, pale yellow leaflets of π-sulphur (S_π) crystallises out. This is a S$_6$-molecular species.

At its boiling point, sulphur forms a red vapour which turns yellow with the rise in temperature. It is believed that the sulphur vapour is made up of a varying proportion of S_8, S_6 and S_2 species, the proportion of the low molecular weight species increasing with the rise in temperature. If the vapour at 1100°C is suddenly chilled, a purple paramagnetic solid, with a formula of S_3, is obtained. It is believed that it has a structure similar to that of O_3. Most of the changes described above are represented schematically in Fig. 17·7

Physical properties of sulphur (α-sulphur) : It is a yellow solid, freely soluble in CS$_2$, but sparingly soluble in alcohol and ether, and is insoluble in water. It is odourless and its vapour possesses germicidal and antifungal properties.

Chemical properties of sulphur : The more important chemical properties of elemental sulphur are manifested in its reactions given



above in a schematic manner. Reactions (2) and (5) occur when hydrogen gas and Cl$_2$ gas are bubbled through molten sulphur.

Reactions (6), (7) and (12) take place on heating the components to a high temperature. Reactions (8) and (9) take place on heating sulphur with the concentrated acids, and the reactions (10) and (11) take place a little above the room temperature.

Uses of sulphur : Sulphur is widely used in industry as well as in daily life. Its more important uses are : (1) as a germicide and fungicide for disinfection of houses, (2) in medicine and soaps for external application, (3) in dye industry, (4) for vulcanizing rubber, (5) for the industrial production of sulphur dioxide, sulphuric acid, carbon disulphide, gun powder, safety matches etc.

Compounds of sulphur.

Sulphides : These are binary compounds involving sulphur and a metal possessing rather complex structures. The sulphides are generally obtained by (i) direct combination of sulphur with metals at elevated temperatures and (ii) by the action of H_2S on solutions of metal compounds :

$$Fe+S \xrightarrow{\text{heat}} FeS\ ;$$

$$2Na+S \xrightarrow{\text{heat}} Na_2S\ ;$$

$$HgCl_2+H_2S \xrightarrow[\text{solution}]{\text{in acidic}} \underset{\text{black}}{HgS\downarrow} +2HCl\ ;$$

$$2BiCl_3+3H_2S \longrightarrow \underset{\text{brown}}{Bi_2S_3\downarrow} +6HCl\ ;$$

$$ZnSO_4+H_2S \xrightarrow[\text{solution}]{\text{in alkaline}} ZnS\downarrow +H_2SO_4.$$

The sulphides of Gr.IA and IIA are definitely ionic in character, and are soluble in water, giving rise to the S^{2-} ions. Since H_2S is a very weak acid (and hence S^{2-} is a strong base), these sulphides (which may be considered as the salts of weak acid, H_2S, and the strong bases, the hydroxides of Gr.IA and IIA metals) are extensively hydrolysed in aqueous solution. The solutions react alkaline and smell of H_2S :

$$Na_2S+2H_2O \rightleftharpoons 2NaOH+H_2S.$$

$$(Na_2S \rightleftharpoons 2Na^+ + \underset{\text{(strong base)}}{S^{2-}}\ ; \qquad S^{2-}+2H_2O \rightleftharpoons H_2S+2\,OH^-)$$

The sulphides of the other metals possess considerable covalent character. Since sulphur is much less electronegative than oxygen, the M—S bond is much more covalent than the M—O bond. Also, the much larger volume of the S^{2-} ion (compared to that of the O^{2-} ion, both of which have the same charge) makes it much more polarizable than the O^{2-} ion (see Fajan's rules, Vol. I, Ch. III, pp. 170-172). Thus, the M^{+2} and M^{+3} cations polarize the sulphide ion to a much greater extent and thereby induce more covalent character to the sulphides.

Most of the sulphides, especially those possessing considerable ionic character, react with non-oxidising protonic acids like HCl and H_2SO_4 to liberate H_2S :

$$Na_2S+2HCl = H_2S\uparrow+2NaCl\ ;$$

$$FeS+H_2SO_4 = H_2S\uparrow+FeSO_4.$$

Some sulphides do not react with the above acids, but dissolve in hot nitric acid, forming the metal nitrates, nitric oxide and sulphur : $3CuS+8HNO_3=3Cu(NO_3)_2+2NO+3S\downarrow+4H_2O$.

Some other sulphides (HgS, CoS, NiS) dissolve in hot concentrated HCl in presence of potassium chlorate, or in aqua-regia, liberating sulphur :

$$NiS+2HCl+[O]=NiCl_2+S\downarrow+H_2O.$$

Arsenic, antimony and tin sulphides dissolve in yellow ammonium sulphide, producing the corresponding thio-compounds, which indicates their acidic character :

$$M_2S_3+3(NH_4)_2S+2S \rightarrow 2(NH_4)_3MS_4.$$

$$(M=As\ or\ Sb.)$$

A few transition metals form sulphides with variable stoichiometry, e.g. FeS, FeS_2, CoS, CoS_2 etc. Some of these metal-sulphides may be regarded as non-stoichiometric compounds, e.g. CrS.

Hydride : Sulphur forms only one stable hydride, H_2S, which is called hydrogen sulphide or sulphuretted hydrogen. H_2S can be conveniently generated by the action of dilute acids on metal sulphides like FeS : $FeS+H_2SO_4=H_2S+FeSO_4$. A ready and steady supply of H_2S can be arranged with a Kipp's apparatus, using the above ingredients. H_2S can also be generated in the laboratory by the action of water on **thioacetamide,** C_2H_5NS :

$$CH_3CSNH_2+H_2O \rightarrow CH_3CONH_2+H_2S.$$

H_2S can be purified by cooling the gas (obtained from the Kipp's apparatus) in liquid air, when H_2S gets solidified, leaving the chief impurity, hydrogen, in the gaseous state. This is now pumped out and the solid, on gradual warming, yields pure H_2S.

H_2S is a colourless gas with the smell of rotten eggs and is highly poisonous. It is slighty heavier than air. It is moderately soluble in water and the aqueous solution is acidic.

H_2S burns in air or oxygen and the product is elemental sulphur or sulphur dioxide, depending on whether the supply of air is limited or in excess respectively :

$$2H_2S+O_2 = 2S+2H_2O\ ;$$
$$2H_2S+3O_2 = 2SO_2+2H_2O.$$

It is a fairly strong reducing agent and its reducing character is primarily due to the oxidation of S^{2-} ion into elemental sulphur. In acid solution, the E° of the couple, $S+2H^{+}+2e \rightleftharpoons H_2S$ is $+0{\cdot}14$ volts and hence, it can be oxidised by many oxidants.

(i) It reduces ferric iron into the ferrous state in acid solution : (E° of Fe^{+3}/Fe^{+2} in 1(N)HCl$=+0{\cdot}70$ v) :

$$2FeCl_3+H_2S=2FeCl_2+S\downarrow+2HCl,$$
$$(2Fe^{+3}+S^{2-} \rightarrow 2Fe^{+2}+S^{\circ}\downarrow)$$

(ii) It reduces halogens to the corresponding halides :

$$H_2S+X_2=2HX+S\downarrow \quad (X=Cl, Br).$$
$$(S^{2-}+X_2 \rightarrow 2X^{-}+S^{\circ}\downarrow).$$

(iii) It reduces acidified potassium dichromate (orange) to the green chromic chromium (E° of $Cr_2O_7^{2-}/2Cr^{+3}=1{\cdot}36$ v) :

$$K_2Cr_2O_7+3H_2SO_4+3H_2S=Cr_2(SO_4)_3+3S\downarrow+K_2SO_4+7H_2O.$$
$$(Cr_2O_7^{2-}+14H^{+}+3S^{2-} \rightarrow 2Cr^{+3}+3S^{\circ}\downarrow+7H_2O).$$

(iv) It reduces acidified potassium permanganate solution (pink) to the manganous state (colourless) (E° of MnO_4^{-}/Mn^{+2} in acid solution=1.52 volts).

$$2KMnO_4+3H_2SO_4+5H_2S=2MnSO_4+5S\downarrow+K_2SO_4+8H_2O.$$
$$(2MnO_4^{-}+5S^{2-}+16H^{+} \rightarrow 2Mn^{+2}+5S^{\circ}\downarrow+8H_2O).$$

Hydrogen sulphide in aqueous solution :

In aqueous solution, H_2S is slightly dissociated as : $H_2S \rightleftharpoons H^+ + HS^-$ and thus generates hydrogen ions and reacts acidic. The value of the dissociation constant, $K_1 = \frac{[H^+][HS^-]}{[H_2S]}$, is 9×10^{-8} at 25°C. The bisulphide ion, HS^-, further dissociates as : $HS^- \rightleftharpoons H^+ + S^{2-}$, the dissociation constant, $K_2 = \frac{[H^+][S^{2-}]}{[HS^-]}$, being equal to 1.2×10^{-15} at 25°C. Thus, the overall dissociation constant of H_2S is :

$$K = K_1 \times K_2 = \frac{[H^+][HS^-]}{[H_2S]} \times \frac{[H^+] \times [S^{2-}]}{[HS^-]} = 9 \times 10^{-8} \times 1.2 \times 10^{-15},$$

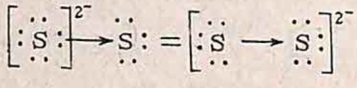
$$\text{or,} \quad K = \frac{[H^+]^2 \times [S^{2-}]}{[H_2S]} = 1.08 \times 10^{-22} \text{ at } 25^\circ\text{C}.$$

Several conclusions can be drawn from the above values and expressions. (*i*) From the values of K_1, K_2 and K, it is clear that H_2S is a very weak acid and the bisulphide ion is a still weaker acid. However, as it generates H^+ ions in solution, it can take part in reactions where H^+ ions are consumed. (ii) In an aqueous solution of hydrogen sulphide H^+, HS^- and S^{2-} ions are in equilibrium with undissociated H_2S and hence, it is also capable of taking part in chemical reaction, characteristic of both the sulphide ion (S^{2-}) and of the bisulphide ion (HS^-). The reaction, $NaOH + H_2S = NaHS + H_2O$, illustrates (i), and the reactions, $NaHS + NaOH = Na_2S + H_2O$ and $CdCl_2 + H_2S = CdS + 2HCl$ illustrate (ii).

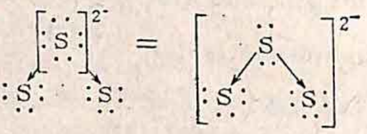
H_2S is widely used as a precipitating reagent in qualitative inorganic analysis. (see vol. I. chapter V, p. 228).

A few other unstable hydrides of sulphur are also known which are discussed under polysulphides.

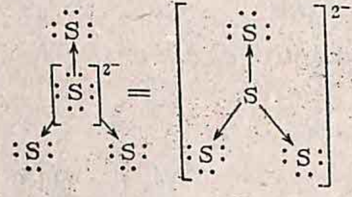
Polysulphides : Free sulphur dissolves in aqueous solutions of alkali metal sulphides or ammonium sulphide, forming yellow solutions containing polysulphides, ranging from disulphides (e.g. Na_2S_2) to the pentasulphide (e.g. Na_2S_5), depending upon the amount of sulphur added. Yellow ammonium sulphide, used in chemical analysis, is a mixture of ammonium polysulphides. As already pointed out, the S^{2-} ion is a strong base and the formation of a polysulphide is the manifestation of the strong Lewis base-character of the sulphide ion, in which the central S^{2-} ion donates one, two, three or four electron-pairs to the corresponding number of sulphur atoms :



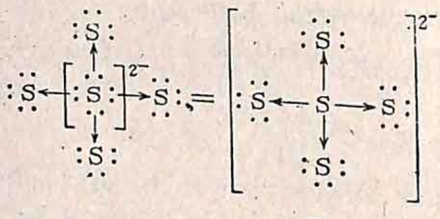
(S_2^{2-}-ion)



(S_3^{2-}-ion)



(S_4^{2-}-ion)



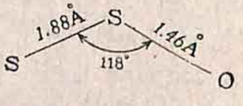
(S_5^{2-}-ion)

On acidification, the polysulphides decompose to sulphide ions and elemental sulphur, which is slowly precipitated.

When a polysulphide solution is slowly added to a dilute acid, a yellow oily liquid is obtained. This oily liquid, on careful fractional distillation, yields fractions consisting of H_2S_2, H_2S_3 and H_2S_5. All these hydrogen polysulphides are unstable, and on warming, decompose to H_2S and free sulphur.

Oxides of sulphur : Sulphur forms several oxides. The following table contains the formulas, names, most important methods of preparation, state of aggregation and the present accepted structure of these oxides :

TABLE 17.5

Formula and name	Method(s) of preparation	State of aggregation etc.	Structure
S_2O Sulphur suboxide or disulphur monoxide	It may be obtained by the passage of silent electric discharge through a mixture of SO_2 and sulphur at 150°—200°C.	It is a colourless gas. Reacts with water, forming H_2S and H_2SO_3.	The structure of S_2O may be represented as : 

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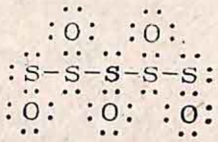
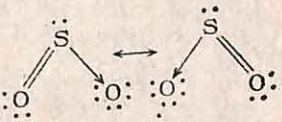
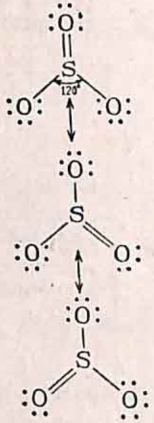
Formula and name	Method(s) of preparation	State of aggregation etc.	Structure
SO Sulphur monoxide	It may be obtained by the thermal decomposition of thionyl chloride at 900°C (or, of thionyl bromide at 500°C), and cooling the product in liquid air.	It is obtained as an orange-red deposit. Reacts with KOH, yielding sulphide, sulphite, and dithionite.	In the vapour state, it is probably dimeric. In the solid state, it is definitely polymeric, possessing the structure 
S_2O_3 Sulphur sesquioxide	It is prepared by the action of sulphur powder and liquid SO_2 under anhydrous conditions.	It is a greenish blue crystalline solid, stable below 15°C. At room temp., it decomposes to S, SO_2 and SO_3.	Its structure is not known with certainty.
SO_2 Sulphur dioxide	(i) Commercially, it is prepared by burning sulphur or roasting sulphide ores in air : $S+O_2=SO_2$, $2ZnS+3O_2=2ZnO+2SO_2\uparrow$. (ii) By the reduction of H_2SO_4 with metals : $Cu+2H_2SO_4=CuSO_4+SO_2\uparrow+2H_2O$. (iii) By decomposing sulphites or bisulphites with acids : $NaHSO_3+HCl=SO_2\uparrow+H_2O+NaCl$. (v) It is also prepared on a large scale by heating a mixture of gypsum and carbon above 1000°C : $2CaSO_4+C=2CaO+2SO_2+CO_2$.	It is a colourless, pungent-smelling and poisonous gas. It is heavier than air and soluble in water, forming sulphurous acid and hence, is the anhydride of sulphurous acid.	It is considered as a resonance hybrid of the following two structures :  Sulphur is in a sp^2-state of hybridisation (with the O–S–O angle of about 120°), with the lone-pair occupying one sp^2-hybrid orbital.

Continued

Formula and name	Method(s) of preparation	State of aggregation etc.	Structure
SO_3 Sulphur trioxide	(i) Commercially, it is generated by the oxidation of sulphur dioxide by oxygen, catalysed by platinised asbestos or vanadium pentoxide : $2SO_2+O_2 \overset{Pt}{\rightleftharpoons} 2SO_3$. (ii) In the laboratory, it can be prepared by distilling conc. H_2SO_4 with P_2O_5 : $H_2SO_4+P_2O_5=SO_3+2HPO_3$.	At room temp., SO_3 is a colourless liquid with an irritating smell. It exists in three forms α, β and γ. It reacts vigorously with water, forming H_2SO_4 and hence, is the anhydride of sulphuric acid.	It is considered as a resonance hybrid of the following three structures : 
SO_4 Sulphur tetroxide	It is obtained by the passage of silent electric discharge through a mixture of SO_2 and excess of oxygen at liquid air temperature and at 0.5 mm. pressure.	At 0°C, it is a white solid, melting to an oily liquid at 3°C. It is a very strong oxidant which oxidises aniline to nitrobenzene.	Its structure is not known with certainty.
S_2O_7 Sulphur heptoxide	It is said to be formed when SO_3 or SO_2 is mixed with excess oxygen and subjected to an electric discharge at low temperatures.	It is said to be a colourless crystalline solid, melting above 0°C, which produces perdisulphuric acid with water.	Not known.

Some important characteristics of a few individual members of the oxides of sulphur.

Sulphur dioxide (SO_2) : It can be easily liquefied at atmospheric pressure by cooling below $-10°$ (ice and salt mixture). The liquid freezes at $-72.7°C$ and boils at $-10°C$. Liquid sulphur dioxide possesses considerable polar character (dielectric constant=13.8 and dipole moment=1.61D), undergoing auto-ionization as $2SO_2 \rightleftharpoons SO^{+2} + SO_3^{2-}$. It is a good solvent for non-metals like sulphur, phosphorus, iodine etc. Sulphites, soluble in liq. SO_2, behave as bases in liquid SO_2 and the thionyl compounds act as acids. Several types of reactions like acid-base reactions, complex formation, precipitation etc. take place in liquid SO_2.

On heating, SO_2 undergoes disproportionation to sulphur and sulphur trioxide :

$$3SO_2 \xrightarrow{1200°C} 2SO_3 + S.$$

Sulphur dioxide can act (in presence of water) both as reducing and oxidising agents, as is evident from the E° values of the following couples : $SO_4^{2-} + 4H^+ + 2e \rightleftharpoons H_2SO_3 + H_2O$; $E° = +0{\cdot}20$ v.

$$H_2SO_3 + 4H^+ + 4e \rightleftharpoons S + 3H_2O \text{ ; } E° = +0{\cdot}45 \text{ v.}$$

It is quite clear from the value of the E° of the first couple that, SO_2 is capable of reducing chemical systems having E° values higher than $+0{\cdot}20$ volts and hence, its reducing character is more important. However, it can also act as oxidising agent towards several chemical systems having stronger reducing character, such as iodide, metallic zinc, hydrogen sulphide etc.

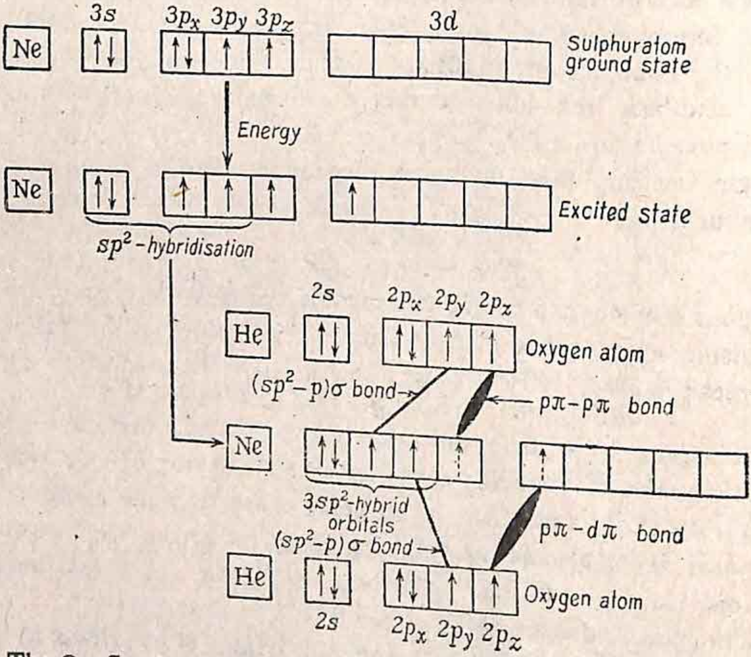
The presence of both reducing and oxidising properties in SO_2 can also be ascribed to the oxidation state of sulphur in SO_2 and also on its electronic configuration. The oxidation state of sulphur in SO_2 is + while the highest oxidation state attainable by sulphur is +6, which SO_2 can do by losing two electrons, and in the process can act as a reducing agent. In the reverse manner, conversion of sulphur in +4 state to the elemental sulphur (S°) can be achieved by the gain of four electrons, in which case SO_2 will act as an oxidising agent.

Sulphur dioxide combines directly with halogens (in presence of camphor catalyst) to form sulphuryl halides : $SO_2 + X_2 = SO_2X_2$ (X=F, Cl and Br). This may be viewed as oxidation of sulphur from +4 to +6 oxidation state.

It reacts with H_2S in the gaseous state, producing elemental sulphur : $2H_2S + SO_2 = 3S + 2H_2O$.

$$[2S^{2-} + SO_2 + 4H^+ = 3S° + 2H_2O]$$

Structure of sulphur dioxide, SO_2 : The hybridisation scheme for the formation and structure of the SO_2 molecule is represented below :



The O—S—O angle is somewhat larger (~128°) than the value of 120° predicted by the sp^2-hybridisation due to lone-pair—bond-pair repulsion.

Sulphur trioxide, SO_3 : All the three forms of SO_3 are chemically almost identical. As already stated, it is a strongly acidic oxide and reacts vigorously with water and basic oxides, liberating much heat and forming H_2SO_4 and sulphates respectively :

$$SO_3+H_2O=H_2SO_4\ ;\ \Delta H=21.3\ \text{Kcals.}$$

$$MgO+SO_3=MgSO_4.$$

It decomposes into sulphur dioxide and oxygen on heating to 1000°C : $2SO_3=2SO_2+O_2$.

It dissolves in concentrated H_2SO_4(~98%), forming fuming sulphuric acid which is technically known as *oleum*. It forms various hydrates in the 0—94% concentration range in various temperature ranges.

It is an oxidising agent which displaces and liberates chlorine, bromine and iodine from their hydracids, and from halides of metals and non-metals.

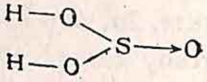
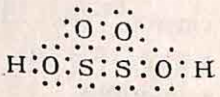
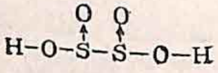
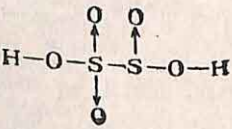
Structure of SO_3 : The structure of SO_3 can be easily visualised from that of SO_2 involving sp^2-hybridisation. In SO_3, the lone-pair of electrons, residing in one of the planar sp^2-hybrid orbitals of the sulphur atom in SO_2, is donated to an empty 2p-orbital (say $2p_z$) of the third oxygen atom in a somewhat excited state, in which all the four 2p-electrons are paired up in the two 2p-orbitals (say, $2p_x$ and $2p_y$) making the third 2p-orbital ($2p_z$ say) empty and ready for accommodating the lone-pair from the sp^2-hybridised sulphur atom in SO_2. The O—S—O angles in this case will be almost 120° due to the absence of lone-pair-bond-pair repulsion present in SO_2.

Oxyacids of sulphur : Sulphur forms quite a number of oxyacids. Table 17.4 contains the names, formulae, most important methods of preparation, state of aggregation etc. and the present accepted structure of these acids. These acids may be divided into four classes : (A) the sulphurous acid group, (B) the sulphuric acid group, (C) the thionic acid group and (D) the peroxysulphuric acid group.

TABLE 17.6

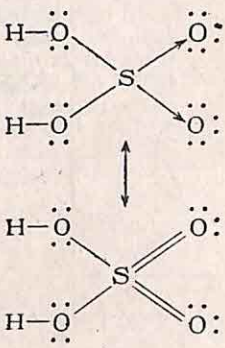
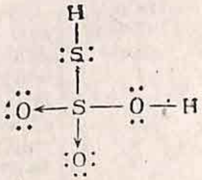
Formula and name	Method of preparation	State of aggregation etc.	Structure
(A) The Sulphurous acid group.			
H_2SO_2 Sulphoxylic acid.	As the cobalt (II) salt, $CoSO_2$, it is prepared by the reaction between sodium hydrosulphite ($Na_2S_2O_4$) and cobalt (II) acetate, followed by the addition of ammonia : $Na_2S_4O_6 + Co(CH_3COO)_2 \rightarrow CoS_2O_4 + 2CH_3COONa$; $CoS_2O_4 + 2NH_3 + H_2O \rightarrow CoSO_2 + (NH_4)_2SO_4$.	The free acid is not known. It is known as its salts. An aqueous solution of the sodium salt is strongly reducing. It is a dibasic acid.	Its structure is not known with any certainty. The probable structure may be represented as : $H:\underset{..}{\overset{..}{O}}:\underset{..}{\overset{..}{S}}:\underset{..}{\overset{..}{O}}:H$ or H—O—S—O—H

Continued

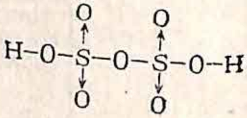
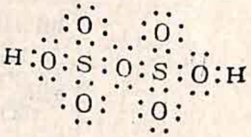
Formula and name	Method of preparation	State of aggregation etc.	Structure
H_2SO_3 Sulphurous acid.	In solution, it is prepared by passing sulphur dioxide in cold water : $SO_2+H_2O=H_2SO_3$.	The pure acid has not been isolated. It behaves as a fairly strong dibasic acid, yielding both acid and neutral salts—the bisulphites and the sulphites. The free acid and both of its salts are fairly strong reducing agents.	The structure of H_2SO_3 is deduced from those of HSO^-_3 and SO_3^{2-} and may be represented as : 
$H_2S_2O_4$ Hyposulphurous acid or dithionous acid.	Reaction of a sulphurous acid solution with zinc amalgam produces hyposulphurous acid : $2H_2SO_3+Zn/Hg \rightarrow H_2S_2O_4+ZnO+H_2O$. The sodium salt is prepared by reducing $NaHSO_3$ by zinc dust : $2NaHSO_3+Zn=Na_2S_2O_4+ZnO+H_2O$.	The free acid is known only in solution; also known as Na-salt. It is a strong reducing agent and is itself easily oxidised into sulphate.	The most probable structure, based on that of its sodium salt, is :  or 
$H_2S_2O_5$ Pyrosulphurous acid.	As an alkali metal salt, it can be prepared by reacting an alkali metal sulphite or bisulphite with SO_2 : $Na_2SO_3+SO_2=Na_2S_2O_5$. It can also be obtained by heating bisulphite : $2NaHSO_3 \xrightarrow{heat} Na_2S_2O_5+H_2O$.	It is known only as salts. It is a dibasic acid, but its acid salt is not known.	The structure of pyrosulphurous acid may be represented as : 

Continued

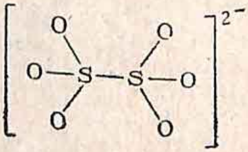
(B) The Sulphuric acid group.

Formula and name	Method of preparation	State of aggregation etc.	Structure
H_2SO_4 Sulphuric acid.	Sulphuric acid is best obtained by (i) catalytic oxidation of SO_2 to SO_3 by oxygen of air, in presence of (a) platinum, (b) V_2O_5 (in the contact process) or nitric oxide (chamber process) : $2SO_2+O_2 \xrightarrow[\text{catalyst}]{450°C} 2SO_3$. (ii) This is then reacted with water present in 98% H_2SO_4 to produce sulphuric acid : $SO_3+H_2O=H_2SO_4$	Pure H_2SO_4 is a colourless, oily liquid of high density (1.84). It is a very strong dibasic acid and exhibits dehydrating and oxidising characteristics along with acidic properties.	The structure of H_2SO_4 may be represented as : 
$H_2S_2O_3$ Thiosulphuric acid.	The free acid is extremely unstable, even in solution. It is best known as its sodium salt, which is obtained by reacting sodium bisulphide (NaHS) with sodium sulphite in aqueous solution : $2NaHS+4NaHSO_3=3Na_2S_2O_3+3H_2O$. The resultant solution, on concentration, yields large colourless crystals of $Na_2S_2O_3.5H_2O$. The free acid can be transiently generated from this Na-salt by the addition of a weak acid like acetic acid.	The free acid undergoes rapid, spontaneous decomposition even in dilute aqueous solution in cold. Sodium thiosulphate is a white crystalline solid, highly soluble in water. It is a fairly strong reducing agent.	The structure of thiosulphuric acid, obtained by extrapolation from the structure of the thiosulphate ion, may be written as :  It is clear from the above structure that the two sulphur atoms are *not* equivalent.

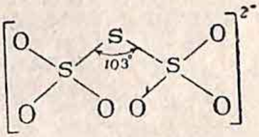
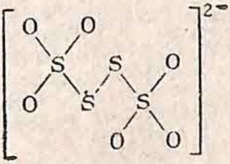
Continued

Formula and name	Method of preparation	State of aggregation etc.	Structure
$H_2S_2O_7$ Pyrosulphuric acid.	It is obtained by dissolving SO_3 in conc. H_2SO_4 : $H_2SO_4+SO_3 = H_2S_2O_7$. It is commercially known as *oleum*. Pyrosulphate salts are obtained by controlled heating of a bisulphate : $2KHSO_4 \overset{heat}{\rightleftharpoons} K_2S_2O_7+H_2O$	It is a viscous, pale brown liquid and behaves as a weak acid. It is converted into ordinary H_2SO_4 on heating due to expulsion of SO_3.	The accepted structure of pyrosulphuric acid is given below :  or 

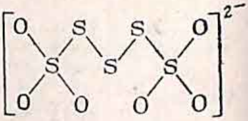
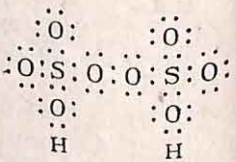
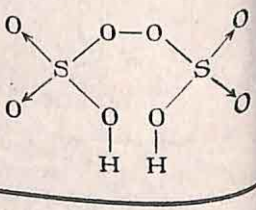
(C) The Thionic acid group (general formula : $H_2S_nO_6$)

Formula and name	Metdod of preparation	State of aggregation etc.	Structure
$H_2S_2O_6$ Dithionic acid.	Though it appears to be the first member of the thionic acid series, according to the general formula $H_2S_nO_6$, it is quite different from the other members, as both the sulphur atoms are present in an oxidation state of 6. As the free acid is not known, it is prepared as dithionate by oxidising sulphurous acid with MnO_2 : $2SO_3^{2-}+MnO_2+4H^+ \rightarrow S_2O_6^{2-}+Mn^{+2}+2H_2O$. An aqueous solution of dithionic acid may be obtained by oxidising H_2SO_3 by ferric nitrate or sulphate.	Pure dithionic acid is not known. It is know in dil. aqueous solution and as salts like $Na_2S_2O_6$. It is a strong dibasic acid. On heating, it is hydrolysed to H_2SO_4 and H_2SO_3 : $H_2S_2O_6+H_2O = H_2SO_4+H_2SO_3$	The present accepted structure of the dithionate ion is :  In this, two SO_3 tetrahedra are linked together by an S–S linkage.

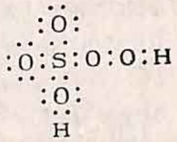
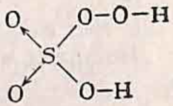
Continued

Formula and name	Method of preparation	State of aggregation etc.	Structure
$H_2S_nO_6$ $n=3, 4, 5$ and 6. Polythionic acids.	Four polythionic acids are well known. These are tri, tetra, penta and hexa thionic acids. All these are obtained as a mixture. (1) By bubbling H_2S through a solution of SO_2 in cold water, when a milky and very complex solution is obtained. This is known as *Wackenroder solution*, and it contains all the polythionic acids. (2) Such a mixture may also be obtained by reducing an aqueous solution of thiosulphate with SO_2 in presence of As (III).	The free acids are rather unstable and decompose spontaneously into sulphur, SO_2 and some sulphate. All of them are known as their alkali metal salts, but no acid-salts are known.	All the polythionic acids are characterised by the presence of one or more sulphur atoms, linked only to other sulphur atoms, and not to any oxygen. Each of the terminal sulphur atoms, however, are connected to three oxygen atoms and are in a sp^3-state of hybridisation.
$H_2S_3O_6$ Trithionic acid.	It may be obtained by the action of $NaHSO_3$ and SO_2 on an aqueous solution of sodium thiosulphate : $Na_2S_2O_3+2NaHSO_3+SO_2 = 2Na_2S_3O_6+H_2O$.	The sodium salt, $Na_2S_3O_6$, is a crystalline white solid, soluble in water. It has mild oxidising properties.	
$H_2S_4O_6$ Tetrathionic acid.	As sodium salt, it is conveniently obtained by, (i) oxidation of thiosulphate by Cu^{+2} ions : $3Na_2S_2O_3+2CuSO_4= Cu_2S_2O_3+2Na_2SO_4 +Na_2S_4O_6$. (ii) By the familiar method of reacting thiosulphate with iodine : $2Na_2S_2O_3+I_2=Na_2S_4O_6 +2NaI$. The free acid can be prepared in aqueous soln. by reacting barium tetrathionate with cold dil. H_2SO_4.	The free acid is fairly stable in dil. aqueous soln. The sodium salts are quite stable and are soluble in water.	

Continued

Formula and name	Method of preparation	State of aggregation etc.	Structure
$H_2S_5O_6$ Pentathionic acid.	It is best obtained by the decomposition of thiosulphuric acid in strongly acid (HCl) solution, below 0°C, in presence of a little arseneous acid : $H_2S_2O_3+H_2O \rightleftharpoons 2H_2SO_2$; sulphoxylic acid $2H_2S_2O_3+H_2SO_2=H_2S_5O_6+2H_2O$.	The free acid is fairly stable in dil. aqueous solution, but decomposes on concentration: $H_2S_5O_6 \rightarrow H_2SO_2+2SO_2+2S$. The reducing property of this acid is due to the sulphoxylic acid generated.	
$H_2S_6O_6$ Hexathionic acid.	It is always produced in the above method of obtaining $H_2S_5O_6$, and may be obtained as the major product by increasing the amount of HCl. It can also be obtained as the potassium salt by the action of KNO_2 on $K_2S_2O_3$ in 12(N) HCl solution below 15°C.	The free acid is unstable even in aqueous solution and decomposes readily when the acidity of the solution is low.	
(D) *The Peroxy sulphuric acid group.* $H_2S_2O_8$ Peroxy disulphuric acid. (Marshall's acid)	It is best obtained by the anodic oxidation of 50% sulphuric acid (or bisulphate) in cold, using a platinum anode and high current density : $H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$ At anode : $2HSO_4^- \rightarrow H_2S_2O_8+2e$. At cathode : $H^+ + e \rightarrow H$; $2H \rightarrow H_2\uparrow$. It can also be prepared by reacting H_2O_2 with chlorosulphonic acid : $2HSO_3Cl+H_2O_2 = H_2S_2O_8+2HCl$.	It is a fairly stable crystalline solid, melting at 68°C. In aqueous soln., it slowly hydrolyses to permonosulphuric acid. It is a strong oxidising agent.	The accepted structure of $H_2S_2O_8$ may be represented as :  or 

Continued

Formula and name	Method of preparation	State of aggregation etc.	Structure
H_2SO_5 Peroxy monosulphuric acid. (Caro's acid)	As mentioned above, it may be obtained by the slow-hydrolysis of $H_2S_2O_8$: $H_2S_2O_8+H_2O = H_2SO_5+H_2SO_4$.	It is a white crystalline solid, fairly stable and melting at 45°C. It is a strong oxidising agent, stronger than $H_2S_2O_8$. It liberates iodine *readily* from KI : $H_2SO_5+2KI=I_2+K_2SO_4+H_2O$.	The structure of H_2SO_5 is represented as :  or 

Some more important aspects of the individual oxyacids of sulphur.

Sulphurous acid, H_2SO_3 : The strongly reducing action of H_2SO_3 is due to the ease of its oxidation to H_2SO_4, which is evident from the redox potential of the couple $SO_3^{2-}+H_2O \rightleftharpoons SO_4^{2-}+2H^++2e$, $E^\circ=-0.20v$. It reduces Cl_2, Br_2 and iodine to their hydracids :

$H_2SO_3+X_2+H_2O=H_2SO_4+2HX$ (X=Cl, Br, I). This reaction is quantitative with iodine and is used for the estimation of sulphurous acid, sulphites and sulphur dioxide.

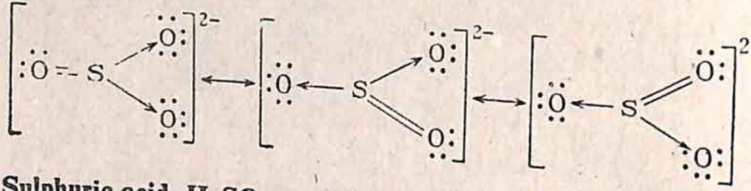
It also reduces acidified iodate solution to iodine : $2KIO_3+5H_2SO_3 = 2KHSO_4+3H_2SO_4+I_2+H_2O$.

With stronger reducing agents, sulphurous acid behaves as an oxidising agent. This is possible because, in H_2SO_3, sulphur is present in an intermediate state of oxidation of +4. This +4 state can go up to the +6 state by the loss of two electrons, under the influence of stronger electron-acceptors or oxidising agents. Again, this +4 state can also come down to the zero oxidation state (in the form of elemental sulphur) by accepting four electrons from stronger electron-donors or reducing agents. This is also evident from the red-ox potential of the couple, $SO_3^{2-}+6H^++4e \rightarrow S+3H_2O$ ($E^\circ=0.45v$).

Thus, H_2S reduces sulphurous acid into elemental sulphur :

$$H_2SO_3+2H_2S=3S\downarrow+3H_2O.$$

The structure of the free acid is not known with certainty. X-ray analysis of alkali metal sulphites indicates that, the SO_3^{2-} ion exists in a pyramidal structure, with the sulphur atom in sp^3-hybridised state. But, the S–O bond-lengths indicate considerable double bond character, which can be explained by the involvement of resonance of the following types :



Sulphuric acid, H_2SO_4 : Sulphuric acid finds innumerable uses in industry and is one of the most important bulk chemicals in use nowadays. It is manufactured by (i) the lead chamber process and (ii) the contact process, of which, the contact process is much more widely used.

When sulphuric acid of about 98% (or less) strength and of average purity is required, the chamber process can be applied. However, if 100% H_2SO_4 of high purity is wanted, the contact process must be used. We shall now briefly outline the chemical principles involved in the chamber process and then discuss the chemical principles of the contact process in more details.

The chamber process : Sulphur dioxide, obtained by burning sulphur or iron pyrites, after proper purification, is allowed to react catalytically with a mixture of nitric oxide (obtained by heating $NaNO_3$ with conc. H_2SO_4) and oxygen (from air) inside chambers lined with lead sheets (and hence the name, the chamber process) when SO_2 is oxidised to SO_3. The exact nature of reactions taking place inside the chambers is not known with certainty. The following reactions represent a plausible pathway :

$$2NO+O_2 \rightarrow 2NO_2\ ;$$
$$SO_2+H_2O \rightarrow H_2SO_3\ ;$$
$$H_2SO_3+NO_2 \rightarrow \underset{\text{sulphonitronic acid.}}{H_2SO_5N.}$$

This H_2SO_5N species can react in two different ways :

(i) $2H_2SO_5N+NO_2 \rightarrow 2NOHSO_4+NO+H_2O$; (nitrosyl bisulphate) ;

(ii) $H_2SO_5N \rightleftharpoons H_2SO_4+NO$.

Again, nitrosyl bisulphate can react in two ways :

(a) $2NOHSO_4+SO_2+2H_2O=2H_2SO_5N+H_2SO_4$

and (b) $4NOHSO_4+2H_2O=4H_2SO_4+4NO+O_2$. Nitric oxide and oxygen, produced in the last reaction forms NO_2 again and the cycle goes on. [This mechanism accounts for the formation of nitrosyl bisulphate as an intermediate product, and also the production of nitric oxide and oxygen in the final stage. This nitric oxide and oxygen again form NO_2, which effects oxidation of SO_2 to SO_3 and the cycle goes on.]

Sulphuric acid obtained by the chamber process is generally of a concentration of ~ 80% and is not very pure. The acid is further purified and then concentrated by the *Cascade* process or *Gillard* process. A purified chamber-acid of ~ 98% strength is used in the contact process for absorption of SO_3.

The contact process : Most of the production of sulphuric acid is done by this process, which is based on the *catalytic oxidation* of very pure SO_2 to SO_3 by the oxygen of air. The reaction involved is :

$$\underset{2\text{ vols. }1\text{ vol.}}{2SO_2+O_2} \rightleftharpoons \underset{2\text{ vols.}}{2SO_3} ; \triangle H=-45.2 \text{ Kcals.}$$

Like the reaction involved in the synthesis of ammonia in the **Haber process,** this reaction also is a *reversible* and *exothermic* reaction, in which *contraction in volume* takes place due to the forward reaction.

Physico-chemical principles are similar to those involved in the ammonia synthesis from hydrogen and nitrogen (see Vol. II, p. 115-117) and the following comments can be made :

Effect of temperature : As the reaction is exothermic, better yield is obtained at lower temperatures. However, to strike a balance between the loss in yield due to the raising of the reaction temperature, and the economic gain due to the reduction of the time of manufacture for the same reason, an *optimum temperature* of 400° – 450°C is used, when either platinised asbestos or vanadium pentoxide is used as a catalyst.

Influence of catalyst : Just as in the case of ammonia manufacture, the rate of conversion of SO_2 to SO_3 (at the optimum temperature range) is tremendously influenced by suitable catalysts. The two catalysts generally used are : (i) platinised asbestos or, (ii) vanadium pentoxide. The platinum catalyst is expensive, but is very efficient and effect almost 100% conversion of SO_2 to SO_3. However, in this case, the SO_2 must be very pure, as the catalyst is easily poisoned by the presence of even trace amounts of arsenic and other impurities.

Effect of pressure : From stoichiometry of the reaction

$$2SO_2+O_2 \rightleftharpoons 2SO_3,$$

it is evident that, higher pressure will lead to better yield, as the volume is decreased due to the forward reaction. However, due to the very high efficiency of the catalysts used, the use of higher pressure becomes superfluous. Also, application of higher pressure involves various technical difficulties and enhances the production cost. Thus, in actual practice, the reaction is performed under ordinary pressure.

The effect of concentration : It is quite obvious that the rate of the forward reaction will increase with the increase in concentration of the reactants. In practice, the concentration of oxygen is increased by increasing the $O_2 : SO_2$ ratio by admitting more air.

Raw materials : The materials required are : (i) elemental sulphur or iron pyrites as the source of sulphur ; (ii) air, as the source of oxygen ; (iii) 98% H_2SO_4 to absorb the pure SO_3 and (iv) the catalyst.

Sulphur dioxide is generated by burning sulphur or iron pyrites in calculated excess of air (so as to maintain the desired $O_2 : SO_2$ ratio) and is passed through a purifying system consisting of : (i) dusting chamber, where the gas is freed from dust particles ; (ii) cooling coils to remove condensable impurities ; (iii) scrubbing tower (to remove washable impurities ; (iv) drying tower (to dry the wet gases from scrubbing tower ; (v) arsenic purifier (to remove arsenical impurities completely and (vi) finally, the gas is passed through a glass box where *tyndal effect* is utilised to check the presence of suspended impurity, if any.

The pure synthesis gas, containing SO_2 and O_2, is then passed through a pre-heater maintained around 450°C and then led into the *contact chamber*, consisting of a series of iron tubes packed with the catalyst, which is either platinised asbestos or vanadium pentoxide (sodium vanadate is also used by some manufacturers). The temperature of the catalyst chamber is maintained at about 450°C by regulating the flow of the (SO_2+O_2) gas mixture through it. As the reaction is exothermic no external heating is required after the reaction is started.

The gases leaving the contact chamber, consisting of SO_3 and O_2, are then sent up in the *absorption tower*, where a descending stream of 98% acid (usually obtained by the purification and concentration of chamber acid) meets the sulphur trioxide gas going up and absorbs it yielding pyrosulphuric acid ; $H_2SO_4+SO_3 \rightarrow H_2S_2O_7$. This is commercially known as *oleum*. Sulphuric acid of any desired strength can be obtained by proper dilution of this oleum :

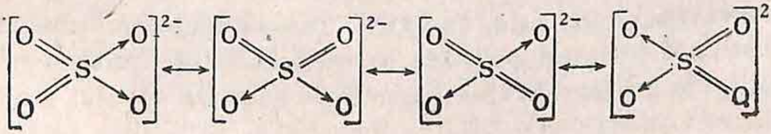
$$H_2S_2O_7+H_2O=2H_2SO_4.$$

The efficiency of the platinum catalyst is no doubt greater than that of the V_2O_5 catalyst, but it is very expensive and is easily poisoned. The V_2O_5 catalyst, on the other hand, is much cheaper and is not poisoned easily. Hence, V_2O_5 is now being used on a much wider scale.

Instead of water, 98% H_2SO_4 is used for the absorption of SO_3, because it produces a dense white fog with water which is very difficult to remove.

Apart from the few characteristic properties of sulphuric acid mentioned in Table 17.4, the following are of considerable importance : Being a strong dibasic acid, it forms both the acid salts or bisulphates (i.e., $MHSO_4$, where M=Na, K etc.) and the normal salts or sulphates.

In aqueous solution, sulphuric acid is the second strongest acid ; $HClO_4$ is slightly stronger than H_2SO_4. Even nitric acid behaves as a base in pure sulphuric acid. The sulphate ion SO_4^{2-} is tetrahedral with the sulphur in a sp^3-hybridised state. The S—O bond-lengths exhibit considerable shortening from the calculated S—O single-bond distance, which is explained by the resonance between single and double bonds :



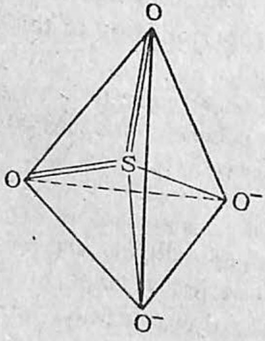
Thiosulphuric acid and thiosulphates : As its sodium salt $Na_2S_2O_3.5H_2O$ (commercially known as *hypo*), thiosulphuric acid finds wide use in photography (as a fixer) due to its capacity of forming soluble silver complexes, whereby it dissolves out unreacted silver halides from ordinary and X-ray photographic plates :

$$2AgX+4Na_2S_2O_3=2Na_3\underset{\text{soluble}}{[Ag(S_2O_3)_2]}+2NaX.$$

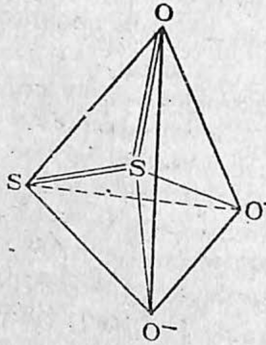
It is also used in volumetric analysis involving iodine (iodimetry and iodometry) :

$$2Na_2S_2O_3+I_2=Na_2S_4O_6+2NaI.$$

It also finds some uses as a mild reducing agent. Structurally, the thiosulphate and the sulphate ions are similar to each other. The $S_2O_3^{2-}$ ion may be considered to be derived from the SO_4^{2-} ion by the replacement of one oxygen atom by a sulphur atom :



(*a*)
The SO_4^{2-}-ion



(*b*)
The $S_2O_3^{2-}$-ion

It is also clear from the above structure of the $S_2O_3^{2-}$ ion that, the two sulphur atoms are not equivalent, and in the reaction

$$S_2O_3^{2-}+H^+\rightarrow HSO_3^-+S\downarrow,$$

the terminal sulphur atom (on the left side corner of the tetrahedron in fig. *b*) is cleaved off, leading to the formation the bisulphite ion. Thus, in the $S_2O_3^{2-}$ ion, the central sulphur atom is in the sp^3-hybridised state.

Peroxydisulphuric acid, $H_2S_2O_8$: This is best considered as a derivative of hydrogen peroxide in which both the hydrogen atoms of H_2O_2 are replaced by the sulphonic acid group (SO_3H), keeping the peroxo moiety (—O—O—) intact.

Method of preparation : Peroxydisulphuric acid is best obtained by the electrolysis of a concentrated solution of H_2SO_4 at or below 0°C. The anodes are of thin strips of platinum, and a high current density is essential. Under these conditions, sulphuric acid largely remains as bisulphate ion, HSO_4^-, which migrates to the anode compartment of the electrolytic cell, kept immersed in a freezing mixture. The electrochemical reaction involved is anodic oxidation and may be represented as follows :

$$H_2SO_4 \rightleftharpoons \underset{\substack{\downarrow \\ \text{to} \\ \text{cathode}}}{H^+} + \underset{\substack{\downarrow \\ \text{to anode}}}{HSO_4^-}$$

$$2HSO_4^- \rightarrow H_2S_2O_8 + 2e.$$

The free acid is not stable and undergoes hydrolysis to the peroxymonosulphuric acid. Hence, the ammonium salt, $(NH_4)_2S_2O_8$, which is stable, is commercially obtained by the electrolysis of 20 – 30% ammonium sulphate or bisulphate under conditions similar to those used in the preparation of the acid.

Permonosulphuric acid, H_2SO_5 : This may be considered as the derivative of H_2O_2 in which only one hydrogen atom is replaced by one sulphonic acid (SO_3H) group.

Method of preparation : It is obtained by the hydrolysis of the peroxydisulphuric acid and hence, the same method is applied for its preparation. The $H_2S_2O_8$ is then allowed to stand, when it hydrolyses to the peroxymonosulphuric acid as :

$$H_2S_2O_8 + H_2O = H_2SO_5 + H_2SO_4.$$

If the temperature of the solution is raised, or more time is allowed to elapse, the permonoacid further hydrolyses to hydrogen peroxide :

$$H_2SO_5 + H_2O = H_2SO_4 + H_2O_2.$$

This forms the basis of the technical method of manufacturing hydrogen peroxide.

Peroxysulphuric acids and peroxysulphates are some of the strongest oxidising agents, as is evident from the following E° value :

$$S_2O_8^{2-} + 2e \rightarrow 2SO_4^{2-},\ E^\circ = 2.01\ \text{v}.$$

The $S_2O_8^{2-}$ ion liberates iodine from iodides in aqueous solution :

$$S_2O_8^{2-} + 2I^- + 2H^+ = 2HSO_4^- + I_2.$$

Ferrous salts are oxidised by $S_2O_8^{2-}$ to the ferric state and manganous salts to MnO_2 in aqueous solution. But, in presence of silver ions, Mn^{+2} is oxidised to permanganate :

$$Mn^{+2}+S_2O_8^{2-} \xrightarrow{Ag^+} MnO_4^-.$$

This catalytic activity of Ag^+ is due to the generation of Ag^{+3} by $S_2O_8^{2-}$, which then oxidises Mn^{+2} to MnO_4^- and itself is again reduced to Ag^+.

Halogen derivatives of oxides and oxyacids of sulphur.

1. **The oxyhalides :** The more important oxyhalides of sulphur may be grouped under two headings : (a) Thionyl or sulphinyl-halides, SOX_2 (where X=F, Cl and Br). (b) Sulphuryl or sulphonyl halides, SO_2X_2 (where X=F, Cl). Another type of oxyhalide e.g. pyrosulphuryl halide, is also known, but is of no importance.

Thionyl Chloride, $SOCl_2$: This can be obtained by (i) passing dry SO_2 over PCl_5. $SO_2+PCl_5=SOCl_2+POCl_3$.

(ii) By heating sodium sulphite with PCl_5 at ~150°C.

$$Na_2SO_3+2PCl_5 = SOCl_2+2POCl_3+2NaCl$$

$SOBr_2$ can be prepared by the above methods, replacing PCl_5 by PBr_5, and SOF_2 is obtained by treating $SOCl_2$ with SbF_3.

$SOCl_2$ is a colourless, heavy liquid with a pungent smell, boiling at 78°C. It is rapidly hydrolysed by water to HCl and H_2SO_3 :

$$SOCl_2+2H_2O=H_2SO_3+2HCl.$$

This is the basis of its use for the preparation of anhydrous transition metal halides from the corresponding hydrated salts. It reacts vigorously with different types of OH groups of organic compounds, replacing it with a chlorine :

$$R-OH+SOCl_2 = R-Cl+SO_2+HCl\ ;$$

$$R-COOH+SOCl_2 = RCOCl+SO_2+HCl.$$

Uses : It is extensively used for chlorination of organic compounds by he replacement of any type of OH group present.

Thionyl chloride has a pyramidal structure with the sulphur atom in the sp^3-state of hybridisation, with the sulphur atom at the centre, the oxygen and the two halogens occupying the three corners, while the lone-pair on sulphur occupies the fourth corner. The tetrahedron is distorted to the pyramidal form, due to the lone-pair–bond-pair repulsion.

Sulphuryl chloride, SO_2Cl_2 : This can be prepared by the direct combination of SO_2 with chlorine in presence of a catalyst like charcoal or camphor : $SO_2+Cl_2 = SO_2Cl_2$.
It is a colourless fuming liquid with a pungent smell. It forms a colourless crystalline pentahydrate with ice-cold water.

It is used as a chlorinating agent in orgainc industries such as, dye-stuffs, cellulose-based synthetic fibres, pharmaceuticals, and pesticides.

The halogenated oxyacids : The halosulphonic acids, HSO_3X (X=F and Cl) are the only members of real importance.

Chlorosulphonic acid, HSO_3Cl : It can be obtained by (i) the action of dry HCl on sulphur trioxide or fuming sulphuric acid : $SO_3+HCl=HSO_3Cl$. (ii) It can also be obtained by reacting $POCl_3$ with strong H_2SO_4 : $2H_2SO_4+POCl_3=2HSO_3Cl+HPO_3+HCl$. The sulphuryl halides may be regarded as derivatives of H_2SO_4, in which one OH group is replaced by a halogen. It is a colourless fuming liquid and is used as a chlorinating agent in organic synthesis.

Fluorosulphonic acid may be prepared by the action of conc. HF on dry SO_3 : $SO_3+HF = HSO_3F$.
It is a colourless liquid and forms salt with alkali halides :

$$HSO_3F+NaCl=NaSO_3F+HCl.$$

SELENIUM AND TELLURIUM

Selenium and tellurium are the two heavier members of Gr.VIB, and according to the general trend within a particular sub-group, they exhibit close chemical similarity among themselves. Hence, the chemistry of Se and Te is best discussed together. Both of them occur together in sulphide ores, specially in *copper pyrites*.

Extraction of Se and Te : The major commercial source of Se and Te is the *anode slime* of copper refining by the electrolytic method. The *anode slime* is slowly deposited in the canvas bags enclosing the impure copper anodes, and contain 1.5 to 9% Se, 0.8 to 6% Te and the rest Cu, Ag, Au and some useless sludge. This anode slime is subjected to certain chemical treatments, as a result of which, selenium and tellurium are separated. The actual steps involved in the process are briefly outlined below :

Step I. Roasting : The anode slime is mixed with conc. H_2SO_4 and some $NaNO_3$ and roasted in air at 400 – 450°C. All the copper is converted into water-soluble $CuSO_4$, while selenium (about 80% of total selenium-content) is oxidised to SeO_2, which sublimes out of the solid roasted mass at 315°C and is allowed to pass into water, when selenious acid, H_2SeO_3, is formed. Some impure selenium is also precipitated and is filtered off. The filtrate is stored for the extraction of Se (**Solution A**).

Step II. First alkali extraction : The roasted slime, containing all the tellurium, the remaining selenium and all copper as copper sulphate, is extracted with water to remove copper sulphate. The residue is then vigorously agitated with hot 10% NaOH, when ~98% of tellurium and some portion of the remaining selenium dissolves :

$$3Te+6NaOH=2Na_2Te+Na_2TeO_3+3H_2O\ ;$$
$$3Se+6NaOH=2Na_2Se+Na_2SeO_3+3H_2O.$$

This is then filtered, the filtrate is boiled with H_2SO_4, and air is bubbled through the boiling solution, when tellurium is precipitated as TeO_2 (**Residue A**), while selenium remains in solution as H_2SeO_3. It is filtered and the filtrate (**Solution B**) is kept for the recovery of selenium.

Step III. Alkali fusion : The residue obtained after the first alkali extraction, still contains some Te and Se. It is mixed with silica and sodium carbonate and fused in a reverberatory furnace. To the molten mass, some scrap iron is added. A slag is formed which contains most of the remaining Se and Te, and it floats up.

Step IV. Second alkali extraction : The above slag is taken off, allowed to solidify and extracted with the mother-liquor (of NaOH) from step II. This dissolves out the Se and Te present in the slag. It is filtered and the residue is rejected. The filtrate is then treated with H_2SO_4, when TeO_2 is precipitated (**Residue B**), leaving a little selenium in solution (**Solution C**).

$$Na_2TeO_3+H_2SO_4=TeO_2+Na_2SO_4+H_2O.$$

Recovery of selenium : (A), (B) and (C) are mixed together and boiled with potassium nitrate, when H_2SeO_3 gets oxidised to selenic acid. H_2SeO_4 : $H_2SeO_3+[O]=H_2SeO_4$. This is precipitated on concentration. It is filtered and then boiled with conc. HCl, when it is reduced to selenous acid again :

$$H_2SeO_4+2HCl=H_2SeO_3+H_2O+Cl_2.$$

SO_2 gas is then bubbled through the hot solution containing H_2SeO_3, when crude selenium is precipitated as a red powder :

$$H_2SeO_3+2SO_2+H_2O=Se\downarrow+2H_2SO_4.$$

Purification of Se : This crude, powdered selenium is mixed with the other portion of Se, obtained in the first step, and washed thoroughly with water and then dried. The dry crude is then distilled in retorts, made of iron, when selenium of 99·8% purity distills off.

Recovery of tellurium : The residues (A) and (B) are mixed together and reduced by heating with carbon :

$$TeO_2+2C\xrightarrow[\text{heat}]{500°C}Te+2CO.$$

Alternatively, the mixed residue of TeO_2 is dissolved in HCl and SO_2 is passed through the solution, when crude tellurium is precipitated as a dark grey powder :

$$H_2TeO_3+2SO_2+H_2O=Te\downarrow+2H_2SO_4.$$

Purification of tellurium : Crude tellurium (obtained as above) is washed thoroughly with water, dried, mixed with flour and distilled in graphite retorts when tellurium containing less than 0.07% selenium is obtained.

Allotropic modifications of Se and Te : Selenium occurs in *three different forms*. Two different non-metallic modifications, both of which are red in colour and contain Se_8 rings analogous to the S_8 rings (see p. 199). These forms are rather unstable and belong to the monoclinic system. The third variety is the metallic form, grey in colour, containing infinite spiral chains of Se-atoms, in which feeble metallic interaction exists between the adjacent chains. This is the stable variety of selenium and the crystals belong to the hexagonal system (See. vol II, Appendix).

Tellurium is semi-metallic in nature and its stable form is crystalline and silvery white. Structurally, it is similar to grey selenium, but is much more metallic.

Properties of Selenium and tellurium.

Selenium : The stable, grey selenium boils at 685°C and gives off red vapour. Most of its chemical properties are expressed in the schematic representation, "some important reactions of selenium". Its electrical conductivity increases when it is exposed to radiation.

Tellurium : Tellurium is silver-white. Its melting point is 452°C and it boils at 1390°C. Though it has some metallic character, it is a bad conductor of electricity. Its structure is similar to that of selenium. The more important chemical properties are included in the schematic representation, "some important reactions of tellurium."

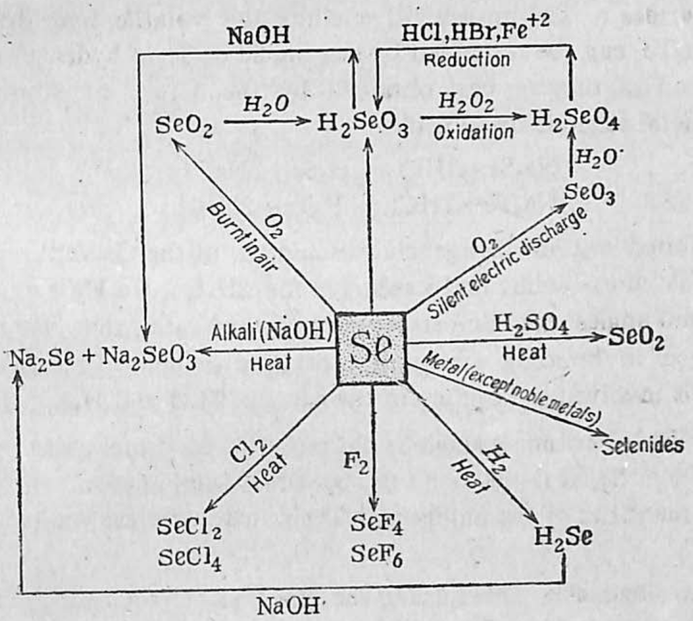
Selenium and tellurium are moderately reactive, slightly less so than sulphur. Some of their more important reactions are schematically represented in page 229.

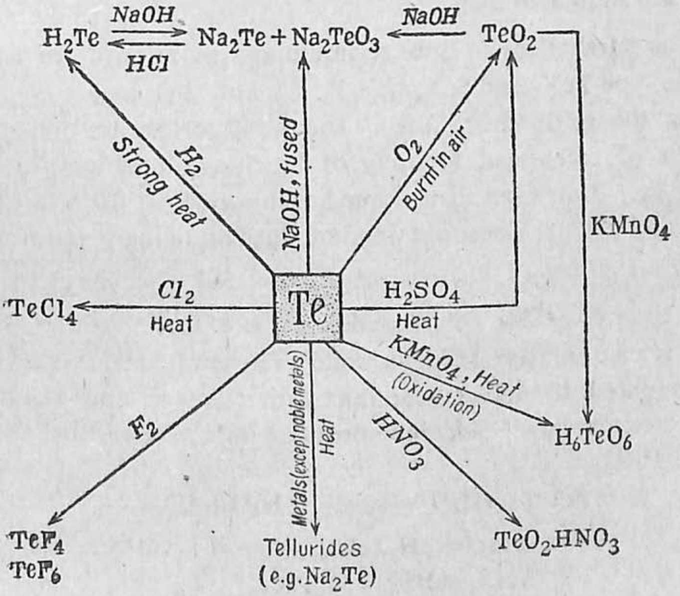
Uses of selenium and tellurium.

Selenium : (1) The largest use of selenium is in the glass industry for the production of the red "ruby glass", by adding 2% selenium along with 1% CdS and 1% As_2O_3. (2) The emission of electrons and increase in conductivity of Se on irradiation, lead to its uses in the manufacture of "selenium cells". (3) It is used in the vulcanization of rubber and (4) is employed as a dehydrogenating agent in organic chemistry.

Tellurium : Very few uses of tellurium have been found. (1) Traces (0·05–0·08%) of tellurium, when present in lead, can improve its corrosion-resistance considerably and increases its tensile strength. (2) A specially prepared tellurium electrode has been used to determine *p*H values of aqueous solutions in the alkaline range (*p*H~9–13), even in presence of mild oxidising agents.

Selenides and tellurides of metals : As indicated in the scheme of reactions below, metal selenides and tellurides are obtained by strongly heating an intimate mixture of selenium or tellurium and a metal, say, sodium : $2Na+Se=Na_2Se$ and $2Na+Te=Na_2Te$. The noble metals do not form such selenides and tellurides.


NaOH
HCl,HBr,Fe+2
Reduction
SeO2
H2O
H2SeO3
H2O2
Oxidation
H2SeO4
H2O
SeO3
O2
Burnt in air
O2
Silent electric discharge
Alkali (NaOH)
Heat
Na2Se + Na2SeO3
Se
H2SO4
Heat
SeO2
Metal (except noble metals)
Selenides
Cl2
Heat
F2
H2
Heat
SeCl2
SeCl4
SeF4
SeF6
H2Se
NaOH


H2Te
NaOH
HCl
Na2Te + Na2TeO3
NaOH
TeO2
H2
Strong heat
NaOH, fused
O2
Burnt in air
KMnO4
Cl2
Heat
TeCl4
Te
H2SO4
Heat
KMnO4, Heat
(Oxidation)
H6TeO6
F2
Metals (except noble metals)
Heat
HNO3
TeF4
TeF6
Tellurides
(e.g. Na2Te)
TeO2.HNO3

Hydrides : The unpleasant smelling and volatile hydrides H_2Se and H_2Te can be obtained by heating Se or Te in hydrogen. But, just like H_2S, they are best obtained by the action of dilute acids on a metal selenide or telluride:

$$Na_2Se + 2HCl = H_2Se + 2NaCl\ ;$$
$$Na_2Te + 2HCl = H_2Te + 2NaCl.$$

As pointed out in the general discussion of the Gr.VIB elements, H_2Te is more acidic and less stable than H_2Se. In H_2Se and H_2Te, the bond angles are almost 90°, which indicates that the orbitals involved in bonding are pure *p*-orbitals instead of the sp^3-hybrid orbitals involved in bonding in the cases of H_2O and H_2S.

Halides. The monohalides : Selenium forms dimeric monohalides of the type Se_2X_2 ($X=Cl$ and Br) by direct combination with calculated quantities of the halogens. Their structures are similar to that of S_2Cl_2.

The dihalides : Dihalides of the type TeX_2 ($X=Cl, Br$) are formed by tellurium only and are obtained by the direct action of stoichiometric amount of chlorine or bromine on tellurium. Structurally, they are similar to SCl_2.

The tetrahalides : Both selenium and tellurium form tetrahalides of the type TeX_4 and SeX_4 ($X=F$, Cl and Br) and only tellurium forms the tetraiodide, TeI_4. The tetrafluorides are prepared by the action of calculated amount of fluorine, diluted with nitrogen, on Se or Te. But, even then, some hexafluoride is formed. However, SeF_4 and TeF_4 are best obtained by the following reactions :

$$SeCl_4 + 4AgF = SeF_4 + 4AgCl\ ;$$
$$TeO_2 + 2SeF_4 = TeF_4 + 2SeOF_2.$$

SeF_4 is a liquid, but TeF_4 is a solid. The tetrachlorides and bromides are prepared by direct reactions with chlorine and bromine. All these are solids. Selenium bromide is unstable and hydrolyses readily :

$$SeBr_4 + 4H_2O = H_2SeO_3 + H_2O + 4HBr.$$

$TeCl_4$ forms the complex, H_2TeCl_6, when it is treated with HCl :

$$TeCl_4 + 2HCl = H_2TeCl_6.$$

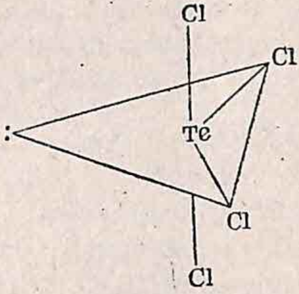
$TeCl_4$ has a trigonal bipyramidal structure (analogous to that of

SCl_4), involving sp^3d-hybridisation, with one position occupied by a lone-pair.

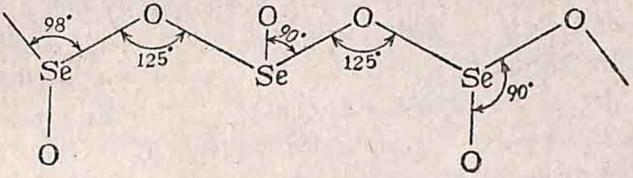
The other tetrahalides are thought to have similar structures.

Hexahalides : Only fluorine brings out the maximum valence of these elements and forms SeF_6 and TeF_6 readily by direct combination with Se and Te.

Oxides. Dioxides : The dioxides, SeO_2 and TeO_2 are obtained by burning the elements in air. Both are solid at room temperature. SeO_2 is a colourless solid, structurally different from that of gaseous SO_2. It is made up of infinite zig-zag chains of selenium and oxygen atoms which are not in the same plane, as is shown below :



$TeCl_4$



TeO_2 is a colourless solid which exists in two ionic forms. SeO_2 is a distinctly acidic oxide which dissolves in water to form selenious acid, H_2SeO_3, and reacts with alkalis to produce tellurites. TeO_2 is less acidic than SeO_2 and is rather amphoteric in character. It is insoluble in water, but reacts with alkalis, producing tellurites :

$$TeO_2 + 2NaOH = Na_2TeO_3 + H_2O.$$

It also dissolves in acids to form basic salts : $TeO_2 + HNO_3 = TeO_2.HNO_3$. These reactions indicate the increase in basic or metallic character of the elements on descending down a Periodic Group.

Selenium dioxide is easily reduced to elemental selenium in strong HCl solution, by reducing agents like SO_2, H_2S, HI, Sn^{+2} etc. TeO_2 is reduced to elemental tellurium on heating with hydrogen or carbon.

Trioxides : When a silent electric discharge is passed through a mixture of selenium and excess of oxygen, selenium trioxide(SeO_3)

is said to be formed. It is a strongly acidic oxide and forms selenic acid, H_2SeO_4, on dissolution in water : $SeO_3+H_2O=H_2SeO_4$.

It reacts directly with alkalis, forming selenates which are isomorphous with sulphates.

TeO_3 is obtained as an orange solid on heating telluric acid, H_6TeO_6 : $H_6TeO_6 \xrightarrow{\text{heat}} TeO_3+3H_2O$.

Above 400°C, TeO_3 decomposes into TeO_2 and oxygen. On prolonged warming with water, it is slowly converted into the ortho-telluric acid, H_6TeO_6. When boiled with concentrated HCl, TeO_3 is slowly reduced to $TeCl_4$: $TeO_3+6HCl = TeCl_4+Cl_2+3H_2O$.

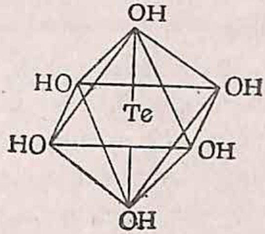
Oxyacids : Selenium forms two oxyacids, selenious acid, H_2SeO_3, and selenic acid, H_2SeO_4, corresponding to sulphurous and sulphuric acids.

Selenious acid, H_2SeO_3 : Selenious acid can be obtained in the free state as a crystalline solid, and is easily prepared by dissolving SeO_2 in water, or by heating selenium with HNO_3. It is a dibasic acid, weaker than H_2SO_3 ($Ka_2=2.4\times10^{-3}$) and forms both acid and normal salts like $NaHSeO_3$ and Na_2SeO_3. H_2SeO_3 is a moderately strong oxidising agent. Structurally, it resembles H_2SO_3.

Selenic acid, H_2SeO_4 : This can be obtained by the oxidation of H_2SeO_3 by H_2O_2 (40%), or by the oxidation of silver selenite, Ag_2SeO_3, by bromine, in aqueous solution : $Ag_2SeO_3+Br_2+H_2O=H_2SeO_4+2AgBr$. The filtrate, on evaporation under vacuum, yields selenic acid as colourless crystals. It is a strong dibasic acid and resembles H_2SO_4 in charring organic matter and in the formation of several hydrates like $H_2SeO_4.H_2O$, $H_2SeO_4.2H_2O$, $H_2SeO_4.4H_2O$ and $H_2SeO_4.6H_2O$. It is a moderately strong oxidising agent and is reduced quantitatively to H_2SeO_3 by HCl, HBr and Fe^{+2} ion. Structurally, it is similar to H_2SO_4, and as said previously, the selenates are often isomorphous with the corresponding sulphates.

Tellurous acid : The free acid has not been properly characterised. TiO_2 reacts with strong alkalis to form tellurites (like Na_2TeO_3) and acid tellurites (like $NaHTeO_3$), from which TeO_2 is precipitated by the addition of acids.

Telluric acid, H_6TeO_6 : Telluric acid, H_6TeO_6, is quite different from sulphuric and selenic acids, and may be obtained from elemental tellurium or TeO_2 by the action of oxidising agents like $KMnO_4$, Ce^{+4}-ions, chromic acid etc. It is best obtained by oxidising a suspension of Te in water with chlorine. After concentration of this solution in vaccum, H_6TeO_6 can be precipitated by the addition of alcohol or acetone. Telluric acid exists as octahedral Te $(OH)_6$ molecules, in which tellurium is present in the sp^3d^2-hybridised state. This may be represented as in the margin :



H_6TeO_6

It behaves as a weak dibasic acid, forming two series of salts like $M^1TeO(OH)_5$ and $M^1_2TeO_2(OH)_4$ · (where M^1=Li, Na). It behaves as a fairly strong oxidising agent.

CHAPTER XVIII

ELEMENTS OF GROUP VII B : THE HALOGENS.

The seventh group of the Periodic Table contains eight elements, *viz.* manganese, technetium, rhenium, fluorine, chlorine, bromine, iodine and astatine. Similar to the other previous groups, this group is also sub-divided into sub-group A and sub-group B, of which the latter is the main sub-group. The sub-group A contains three transitional metals (Mn, Tc and Re), while the sub-group B consists of five **halogens** (meaning *sea-salt producer*), *viz.* fluorine, chlorine, bromine, iodine and astatine. In this chapter, we shall confine our discussions on the elements of the B sub-group only.

Fluorine, chlorine, bromine and iodine are common elements and occur in the earth's crust to the extent of 9×10^{-2} %, 3.1×10^{-3} %, 1.6×10^{-4} % and 3×10^{-5} % respectively. Thus, we find that among the first four elements, the abundance decreases down the group. The last member of this group, *astatine*, is present in minute quantities, being produced by the decay of AcA, ThA and RaA, belonging to the naturally occuring actinium series, thorium series and uranium series (see Vol. I. pp. 204-206). This is a radioactive element and is an α-emitter.

The halogens possess closely related chemical properties, and there exists a very well-marked gradation in them as one passes from one member to another. But, the two end-members, namely fluorine and iodine, display certain peculiarities. Fluorine, as the first member of the group, shows remarkable divergences from the other halogens, both in the elementary state and in the compounds, and as such, it is often called a *super halogen*. All these elements, especially the lighter members, are very reactive. This is attributed to the tendency of their atoms to complete the octet of their outermost electronic shell and thus become singly charged negative ions, and also to the comparatively small value of the energy of dissociation of their molecules into atoms ($X_2\rightleftharpoons 2X$).

The first four halogens are quite familiar. None of them occurs in the free state, but they are available in considerable quantities from concentrated sources in nature. The fifth one (astatine), as already stated, occurs only in small quantities as short-lived radioactive isotopes. Some important properties of the halogens are tabulated in Table 18·1 below :

TABLE 18·1

Property	Fluorine	Chlorine	Bromine	odine
Atomic number	9	17	35	53
Atomic weight	19	35·457	70·916	126·932
Electronic configuration	$\boxed{\text{He}}\ 2s^2 2p^5$	$\boxed{\text{Ne}}\ 3s^2 3p^5$	$\boxed{\text{Ar}}\ 4s^2 4p^5$	$\boxed{\text{Kr}}\ 5s^2 5p^5$
State at 15°C	Gas	Gas	Liquid	Solid
Colour	Pale greenish yellow	Greenish yellow	Dark red	Black (Violet vapour)
Density of solid, g/c.c.	1·3	1·9	3·4	4·93
Atomic volume (c.c.)	14·62	18·66	23·51	25·74
Covalent radius (Å)	0·72	0·994	1·142	·334
Melting point (°C)	−223	−102	−7·3	114
Boiling point (°C)	−187	−34·6	58·78	183
Heat of dissociation of molecules (Kcal/mole)	37·7	56·7	45·2	35·4
Ionisation potential (ev)	17·42	13·01	11·84	10·44
Electron affinity (ev)	3·62	3·79	3·56	3·28
Electronegativity	4·0	3·0	2·8	2·5

The data summarised in Table 18·1 clearly illustrates the regular gradation in some of the important physical properties of the members of the halogen family with the increase of their atomic number or atomic weights, as envisaged in the Periodic law. Gradation in some properties is elaborated as follows :

State of aggregation and colour : All the halogens form diatomic molecules. Their physical state changes from the gaseous to the solid, via the liquid, with the increase in the atomic numbers (or atomic weights) of the elements from fluorine to iodine. Their colour also changes towards darker shades from pale greenish yellow to black, via deep red—in the above order.

Density, atomic volume and atomic radius : Paralleling increases in atomic number or atomic weight, increases in densities of the elements in the solid state, their atomic volumes and covalent radii are clearly exhibited. The melting points and the boiling points of these elements also gradually increase with the increase in their atomic numbers.

Electronegativity : This property of the members of the halogen family decreases down the group with increase in atomic number. Fluorine is the most electronegative, second to none among the elements. In fact, among the halogen oxides, while Cl, Br and I act as the positive component, fluorine behaves as the negative part. The electronegative character of the halogens decreases from fluorine downwards and it is so much weakened in iodine that the electropositive character makes its appearance. This is not only substantiated by the superior affinity of iodine for oxygen, but also by the formation of iodine salts such as $I[ClO_4]$, $[I(py)_2]NO_3$ (py=pyridine) etc., in which the halogen functions as a metal.

Ionisation potential and oxidation states : The electronic configuration ns^2np^5 of the atoms of the halogens immediately suggests its stable oxidation state of -1, and it is amply corroborated by the existence of the whole host of well-defined electrovalent halides. The comparatively large values of the ionisation potentials suggests that, except iodine, the cationic halogen species are highly unlikely. But, there appears to be no bar for these elements to exhibit positive covalencies by sharing electrons with more electronegative elements. In fact, all the halogens, except fluorine, *do* exist in $+1$, $+3$, $+5$, and $+7$ oxidation states. [Fluorine does not exist in positive oxidation state, as there is no element more electronegative than this halogen.] The difference of two units among the various oxidation states, as stated above, is due to the fact that, out of the 7 valence-electrons in any atom of halogen, 6 occur in pairs. The common oxidation states of Gr. VII B elements are shown in Table 18·2. The higher oxidation states arise by the use of *d* orbitals and are found in inter-halogens, halogen oxides and oxyacids.

TABLE 18·2

Element	Oxidation states
Fluorine	-1
Chlorine	$-1, +1, +3, +4, +5, +6, +7$
Bromine	$-1, +1, +3, +4, +5, +6$
Iodine	$-1, +1, +3, \quad +5, +7$

Stability of the halogen molecules : The thermal stability of the diatomic halogen molecules diminishes gradually from fluorine to iodine. The F_2 molecule is very stable ; Cl_2 molecule is only slightly dissociated above 1100°C ; Br_2 molecule is dissociated to the extent of about 6% and I_2 molecule to a large extent below 1000°C.

Oxidising power and Electron affinity : As oxidation is a process in which the oxidising agent gains electrons, the value of electron affinity of an element is a positive index of its oxidising power. All the halogens have large electron affinity values and as such, they are good oxidising agents ; but the oxidising power falls off with increasing atomic number. But, although chlorine has the highest electron affinity value, fluorine is the strongest oxidising agent among the halogens[1]. Thus, fluorine will replace Cl^-, chlorine gas will replace Br^- and bromine, in its turn, will replace I^- from solution. In other words, a halogen of low atomic number will oxidise halide ions of higher atomic numbers.

The reactions of the halogens with water also illustrate the decrease in their oxidising power with the increase in atomic number. Thus, fluorine is such a strong oxidant that it oxidises water to oxygen (and ozonised oxygen) : $2F_2+2H_2O=4HF+O_2$; $3F_2+3H_2O=6HF+O_3$. Chlorine and bromine, however, take part in such reactions very sluggishly due to the high activation energy required. Instead, they readily undergo hydrolysis, $Cl_2+H_2O \rightleftharpoons HCl+HOCl$; $Br_2+H_2O \rightleftharpoons HBr+HOBr$. Iodine is an even weaker oxidising agent and requires the supply of much energy to oxidise water. In fact, under normal conditions, the reverse reaction takes place and oxygen oxidises iodide ions to iodine : $2I^- + 2H^+ + \frac{1}{2}O_2 = I_2 + H_2O$.

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[1] The greater oxidising power of fluorine, as compared to that of chlorine, is due to the fact that the former has lower heat of dissociation and higher heat of hydration than the latter.

Reactivity of the halogens : All the halogens react with many metals and non-metals. Fluorine is the most reactive halogen[2], and there is a gradual decrease in the reactivity on increasing the atomic number of the elements. Due to the high oxidising power of fluorine and chlorine, these two halogens often produce compounds of the other elements in their higher oxidation states, such as in PCl_5, SbF_5, SF_6 *etc.*

(*a*) *Combination with hydrogen : The hydrohalic acids* : The affinity of halogens with hydrogen diminishes from fluorine to iodine. This is also evident from the heats of formation of the respective hydracids as given in the table below. Fluorine combines with hydrogen with explosive violence at low temperatures, even in the dark ; with chlorine, the reaction becomes explosive on exposure to sunlight ; bromine and hydrogen react without any explosion and iodine reacts with hydrogen on heating in presence of platinum catalyst. The hydrogen halides also form an equally well-marked series as shown below :

Some physical properties of hydrogen halides.

TABSE 18·3

Property	HF	HCl	HBr	HI
State of aggregation (15°C)	Liquid	Gas	Gas	Gas
Colour	Colourless	Colourless	Colourless	Colourless
Melting point (°C)	−83	−111·4	−86·9	−50·8
Boiling point (°C)	19·4	−85	−66·7	−35·4
Solubility in water (g/litre)	—	823	2212	2483
Heat of formation (Kcal/mole)	38·5	22	8·0	−6·0

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[2] The superior reactivity of fluorine is due to the combined effect of (i) low dissociation energy of the F_2 molecule, (ii) its high electronegativity, (iii) its extremely high oxidising power and (iv) the very small size of its atom or ion.

It is evident from the heat of formation of the hydrogen halides that their dissociation in the gaseous state would require lower temperatures with the increasing atomic number of the halogen, which is actually the case.

The acid strength of the hydracids (HX) increases with the increase in atomic number from HF to HI, though electronegativity decreases in that direction. This happens because the increase in the size of the halogens with atomic number and the consequent lengthening and weakening of the H$-$X bond which overshadows the opposite effect due to the decrease of electronegativity. This has also been observed in the case of the hydrides of the Gr.VIB elements, *viz*. H_2O, H_2S, H_2Se and H_2Te.*

It may be seen from the table that hydrogen fluoride differs in many ways from the other hydrogen halides. This is due to its greater ionic character and its tendency to associate through hydrogen bonding (See Vol. I, p. 175).

(*b*) *Combination with metals* : Halogens combine with metals to form metallic halides which may be classified as (i) ionic or salt-like halides, (ii) covalent halides and (iii) complex halides. But, there is no strict line of demarcation between the ionic and covalent metal-halides. All variations in properties are due to factors such as the charge and size of the metal ion, the electropositive character of the metal and the electronegative character of the halogen. Thus, in comparing the compounds KCl, $CaCl_2$, $AlCl_3$ and $TiCl_4$, we find regular transition from a purely ionic structure to an essentially covalent structure. Correspondingly, the covalent character of the halides of a particular metal increases with the increasing size and decreasing electronegativity of the halogen. Similarly, on comparing the compounds LiF, LiCl, LiBr, and LiI, or CaF_2, $CaCl_2$, $CaBr_2$ and CaI_2, we find gradual decrease in melting points and changes in other ionic properties (see Vol. I, pp. 169-172). The ionic chlorides, bromides and iodides are generally soluble in water, with solubility increasing with the size of the halide ion. [Although many fluorides are water-soluble, those with very high lattice-energy are insoluble.] For the halides where the bonding is appreciably covalent, the reverse gradation of solubility in water is true.

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* It appears surprising that HF is a weaker acid (in aqueous solution) than other halogen hydracids, although it is of more ionic character and has a greater electronegativity difference between the constituent atoms than the other hydracids. This is mainly due to the fact that the H$-$F bond is much stronger than the H$-$Cl, H$-$Br or H$-$I bonds and the consequent large dissociation energy of the H$-$F bond. The trend in acid strength of the halogen hydracids increases in the order HI>HBr>HCl>HF, which is in conformtiy with the decreasing dissociation energies of the H$-$F, H$-$Cl, H$-$Br and H$-$I bonds. The strength of the H$-$F bond is related to the short bond length of 1·0Å compared with 1·7Å for HI. The weaker character of hydrofluoric acid is also partly due to the association of its molecules through hydrogen bonding.

Electron-donor characteristics : The participation of halide ions in complex formation is well known. They can occupy from one up to all the available co-ordination positions in a complex. Due to the strong electrostatic attraction and high energies of the resulting bonds, fluorine forms quite stable complexes with small electropositive ions like B^{+3}, Al^{+3}, Si^{+4} *etc.* But, as the fluoride ion is not considerably polarizable, it does not form stable complexes with large cations. The more polarizable chloride, bromide and iodide ions yield stable complexes with the large cations, and their stabilities increase in the given order of the halide ions. The maximum co-ordination number of the metal ion in the complex is likely to be attained on the participation of the fluoride ions due to the size-effect.

(*c*) *Oxide formation* : Halogens do not react directly with oxygen. Nevertheless, a large number of halogen oxides are known, which are prepared by indirect methods. Some of the important oxides of the halogens are listed below :

Fluorine	Chlorine	Bromine	Iodine
OF_2	Cl_2O	Br_2O	I_2O_4
O_2F_2	ClO_2	Br_3O_8	I_4O_9
	Cl_2O_6	BrO_2	I_2O_5
	Cl_2O_7		

Of these binary compounds of halogens with oxygen, *the fluorine derivative is better termed as the fluorides of oxygen*, rather than the oxides of fluorine, because of the fact that fluorine is more electronegative than oxygen.

The oxygen compounds of the halogens show the individuality of the elements most vividly. The stability of these compounds are anomalous. Although the bonds in the halogen oxides (except I_2O_4 and I_4O_9) are largely covalent in nature, F_2O is stable while the oxides of chlorine are explosive (some of them violently) ; the oxides of bromine are less stable than chlorine oxides, whereas the oxides of iodine are fairly stable. F_2O dissolves in water to give a neutral solution and as such, it is not an acid anhydride. But, the oxides of other halogens are actually the anhydrides of certain acids which is evident from the nature of their aqueous solution and their reactions with alkalis.

(*d*) *Oxyacids* : The oxyacids are not definitely known for fluorine. All the other halogens form many well-known oxyacids. The stabilities of the oxyacids increase gradually from chlorine to iodine, and for any particular halogen, the stabilities of their oxyacids increase with the increasing number of oxygen atoms in the molecule.

In the oxyacids, the *effective electronegativity* of the central halogen atom is most important in determining the acid strength. As oxygen is more electronegative than Cl, Br and I, larger the number of oxygen atoms attached to the central halogen atom, greater is its effective electronegativity. Thus, the central halogen becomes much more electron-withdrawing and attracts the bond-pair holding the oxygen of the $X-O-H$ group towards itself. This increases the oxygen atom's electron-attracting capacity which pulls the bond-pair of the $O-H$ group towards itself, resulting in a facile release of the H^+ ion. Thus, in the case of a particular halogen, the strength of the oxyacids changes as : $HClO_4 > HClO_3 > HClO_2 > HClO$. Perchloric, iodic and periodic acids are known in the pure state ; but, the other oxyacids are known only in solution or as salts. Chlorine and iodine are the only halogens which give peracids of the type HXO_4 ($X=Cl$ or I). [Iodine forms several condensed forms of periodic acid, and the common one has the unusual formula H_5IO_6.]

(*e*) *Substitution reactions with paraffins and other hydrocarbons* : The gradation in the reactivity of the halogens is well-illustrated in their substitution reactions with the paraffin hydrocarbons. Taking CH_4

as the representative paraffin, it is seen that fluorine attacks it with explosive violence even in the dark to form HF, liberating carbon in the form of soot. With chlorine, similar reaction takes place in direct sunlight; but, in diffused sunlight, the halogen replaces H-atoms of the hydrocarbon one by one to produce CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4. Bromine reacts similarly, but the rate of the substitution reaction is much slower. Iodine is practically without any action on methane under ordinary conditions, due to the reversible nature of the reaction. Iodination of CH_4 takes place only in the presence of certain oxidising agents.

(*f*) *Inter-halogen compounds*: The halogens are capable of forming compounds with one another—each one being able to combine with one or more atoms of any of the other halogens to form the inter-halogen compounds. These are generally formed through the direct union of the halogens, or by the action of a halogen on another lower inter-halogen compound. But generally, there are never more than two different halogens in a molecule. Due to the small electronegativity differences among the halogen atoms, the bonding in these molecules are essentially covalent, and their melting and boiling points increase as the difference in electronegativity increases. In such compounds, the smaller of the two halogens is invariably present in larger quantity, and the larger halogen acts as the central element. As the central halogen increases in size, its covalency, or its ability to accommodate atoms of the other halogen, increases.

(*g*) *Polyhalide formation*: Halide ions often associate with a halogen molecule to form polyhalide ions. Thus, the increased solubility of iodine in an iodide solution is due to the formation of triioide ion: $I_2+I^- \rightarrow I_3^-$. More complex ions like I_5^-, I_7^-, I_9^- have also been prepared. The ability of the formation and the stability of the polyhalide ions are maximum for iodine. The Br_3^- ion is much less stable than I_3^-, and only a few unstable Cl_3^- compounds are reported. Fluorine is not capable of forming F_3^- ion, probably due to the non-availability of *d*-orbitals, which makes the expansion of the octet impossible. Polyhalides of the type, I_2Cl^-, I_2Br^- etc. (which may be termed as heteropolyhalides) are also known.

INDIVIDUAL MEMBERS OF THE HALOGEN FAMILY : FLUORINE

Occurrence : Due to its highly reactive nature, fluorine is never found native. In the combined state, however, the element occurs widely in many minerals such as *fluorspar* (CaF_2), *fluorapatite* $[3Ca_3(PO_4)_2.\ Ca(F, Cl)_2]$, *cryolite* ($Na_3AlF_6$) *etc.*

Isolation : Although hydrofluoric acid was prepared as early as in 1771 (Scheele), the isolation of fluorine was delayed by more than a century due to some inherent difficulties. The method of electrolysis for the preparation of fluorine failed due to the facts that, (i) anhydrous hydrofluoric acid is a non-conductor of electricity, (ii) aqueous solution of a fluoride or hydrofluoric acid produced fluorine during electrolysis no doubt, but the liberated halogen immediately reacted with water to form HF and O_2, (iii) the extreme reactivity of fluorine resulted in its easy combination with the materials of the electrodes and the electrolytic vessels, causing them to get badly corroded, and finally (iv) the deadly poisonous nature of the halogen proved fatal to many scientists, discouraging the effort of working with it.

It was first observed by Gore that potassium hydrogen fluoride (KHF_2) dissolved in anhydrous hydrofluoric acid, and the resultant solution was a conductor of electricity. With this knowledge, Moissan first isolated fluorine (1886) by carrying out the electrolysis of the above mixture in a vessel made of an alloy of platinum and iridium metals, using electrodes of the same material. [This alloy was not attacked by fluorine to any appreciable extent.]

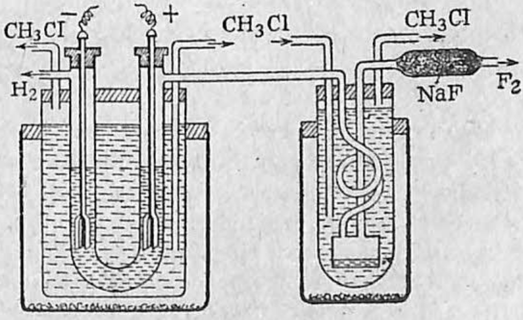

Fig 18·1

Moissan's original method : In 1886, Moissan first isolated fluorine by electrolysing a solution of potassium fluoride in anhydrous hydrofluoric acid. He used a U-tube made of platinum-iridium alloy, with electrodes of the same material, which were insulated by means of stoppers of fluorspar (fig. 18.1). The U-tube was cooled by immersing in a bath of methyl chloride (b.p.=23°C). On electrolysis, fluorine was liberated at the anode and this was successively passed through a platinum spiral tube cooled by liquid methyl chloride (to condense hydrofluoric acid vapours) and then through a platinum tube packed with fused sodium fluoride (to remove last traces of HF). Hydrogen was liberated, as usual at the cathode. [Moissan subsequently used copper vessel with Pt-Ir electrodes for the preparation of fluorine. A protective coating of copper fluoride formed on the inner surface of the vessel prevented the corrosion of the material of the vessel by fluorine.]

Modern method of preparation: Fluorine is nowadays prepared by the electrolysis of fused potassium hydrogen fluoride (m.p.=239°C) at high temperature. Potassium hydrogen fluoride is fused by electrical heating in a V-shaped copper vessel, fitted with graphite electrodes (Fig. 18.2). The electrodes are insulated by means of bakelite cement stoppers. On passing electric current through the molten electrolyte, fluorine gas is liberated at the anode and it is freed from any hydrofluoric acid vapour by passing through two copper U-tubes packed with lumps of fused sodium fluoride. Fluorine is collected in dry glass vessel.

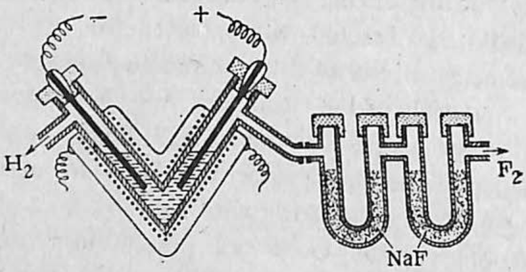

Fig. 18·2

Manufacture of fluorine is best done nowadays by medium-temperature (~100°C) electrolysis of a mixture of 60% KHF_2 and 40% HF. The electrolysis is carried out in a rectangular steel vessel which acts as the cathode, with a graphite rod anode enclosed in a monel metal tube diaphragm. The stoppers and other fittings used in the process are generally made of *teflon*. On passing electric current, fluorine is liberated at the anode and is removed through the monel metal tube and is freed from hydrogen fluoride by passing over fused sodium fluoride. As the electrolysis proceeds, the composition of the electrolyte is carefully regulated by the fresh addition of hydrofluoric acid. The dried gas is compressed, stored and transported in steel or monel metal cylinders.

Properties : Fluorine is a pale yellowish green gas with penetrating and extremely pungent smell. It is highly poisonous. It condenses to a yellow liquid below −187·9°C and freezes to a pale yellow solid at −223°C. Fluorine is the most chemically active element known. It combines directly with almost all elements (except nitrogen and oxygen), to form the corresponding fluorides. Almost all the non-metals (except O_2 and N_2, of course) ignite spontaneously in fluorine. Carbon, phosphorus, arsenic, sulphur, silicon, boron, bromine and iodine burn in fluorine at ordinary temperatures ; chlorine combines with it on heating ; graphite is attacked at red-heat and diamond above 700°C. With moist hydrogen, fluorine reacts with explosive violence even at −252°C in the dark. Most metals (Na, K, Cu, Mg, Sb *etc.*) catch fire in fluorine, others react with incandescence on heating ; gold and platinums react on heating to redness. Fluorine reacts with water to give ozonised oxygen : $2F_2+2H_2O=4HF+O_2$; $3F_2+3H_2O=6HF+O_3$. With dilute alkali solutions, fluorine forms the monoxide (F_2O), while with concentrated alkalis, only oxygen is evolved : $2NaOH\ (dil.)+2F_2 = F_2O+2NaF+H_2O$; $4NaOH\ (conc.)+2F_2=4NaF+2H_2O+O_2\uparrow$. Fluorine displaces the other halogens from their hydracids or halide salts : $2HCl+F_2=2HF+Cl_2$; $2KBr+F_2=2KF+Br_2$ *etc.*

[All these reactions arise from the strong tendency of fluorine to attain the mono-negative valence state by abstracting electrons from all other elements. It has already been stated that fluorine does not react with O_2 and N_2 ; it reacts with Cl_2 only on heating. But, if these elements are present in their negatively charged state, fluorine can abstract from them their excess electrons and liberate them in the elementary state : $2NaCl+F_2=2NaF+Cl_2$; $SiO_2+2F_2=SiF_4+O_2$.]

Hydrofluoric acid (HF).

An aqueous solution of hydrofluoric acid is usually prepared by distilling a mixture of powdered calcium fluoride and conc. H_2SO_4 ($\sim$ 60%) in a lead retort at a temperature of about 300°C. The evolved vapours of hydrogen fluoride are dissolved in water contained in a lead receiver : $CaF_2+H_2SO_4=CaSO_4+2HF\uparrow$. The aqueous solution, containing 40% HF (sp. gr.=1·3), is stored in polythene, gutta-percha or paraffin bottles. [Glass is attacked by hydrofluoric acid.]

Anhydrous hydrofluoric acid is prepared by distilling pure potassium hydrogen fluoride or *Fremy's salt* (KHF_2)* from a platinum or copper retort, using condenser and receiver of the same material. Potassium hydrogen fluoride decomposes into KF and HF on heating. The vapours of HF pass out of the retort through the condenser and are condensed into liquid by cooling the receiver in a freezing-mixture. The colourless liquid is stored in platinum or silver containers.

Anhydrous hydrofluoric acid is a colourless, highly fuming and extremely poisonous liquid (b.p.=19·5°C). It forms ulcerated sores on contact with skin. It is completely miscible with water. Although the anhydrous acid is a non-electrolyte, its aqueous solution conducts electricity. The liquid acid and its vapour consist of polymerised molecules, $(HF)_n$, at low temperatures ; at about 90-100°C, its vapour density agrees with the monomeric formula, HF. Studies by electron diffraction show that the polymeric molecule results from association of HF units through extensive hydrogen bonding and the resultant species has a structure like a zig-zag chain, with H – F – H bond-angle of 134° (see Vol. I. p. 175). The aqueous solution of hydrofluoric acid is very weak ; the degree of dissociation of the acid in a N/10 solution is only 0·015. The aqueous acid attacks glass, by forming hydrofluosilicic acid with silica : $SiO_2+6HF=H_2SiF_6+2H_2O$. [It is, therefore, stored in polythene or gutta-percha bottles, or in glass bottoles coated inside with wax.] Hydrofluoric acid reacts with many metals, forming their fluorides and liberating hydrogen. Unlike the other halogen hydracids, hydrofluoric acid can form acid salts like KHF_2, $NaHF_2$ *etc*. [This is due to the ability of fluorine to form hydrogen bonds. Other halogens are almost incapable of forming hydrogen bonds. See also Vol. I., p. 175.] For this reason, anhydrous sodium fluoride is used to absorb hydrofluoric acid : $NaF+HF=NaHF_2$. Hydrofluoric acid also differs from the other halogen hydracids in that it forms very stable complex acids like fluoboric acid (HBF_4) and hydrofluosilicic acid (H_2SiF_6) on combination with BF_3 and SiF_4.

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* **Preparation of Fremy's salt :** Half the portion of an aqueous solution of HF is neutralised completely with K_2CO_3, and when the evolution of CO_2 has ceased, the other half of the acid is mixed with it. The mixture is then evaporated to dryness and the dried mass is heated for some time at 100°C. The product is kept in a vacuum desiccator over conc.H_2SO_4 to remove last traces of water.

Hydrofluoric acid is used for etching glass and for making metal fluorides. 40 – 60% HF solution is generally used for etching glass. When the solution is used, the etching on glass is clear ; but, if gaseous HF is used, the etching becomes opaque. The acid is also used to remove silica from graphite or iron castings, and also as a reagent in the estimation of silica and a catalyst for some organic syntheses.

Metallic fluorides : These are the metal salts of hydrofluoric acid and are usually prepared by reacting the metal concerned with fluorine or hydrofluoric acid. As fluorine is a highly electronegative element, the simple metallic fluorides are usually ionic compounds. The crystal lattice of all these compounds contain the F^- ion. As the radius of F^- (1·36 Å) is almost identical with that of the oxide, O^{2-}, ion (1·40 Å), many ionic oxides and fluorides have similar formulas and crystal structures as in CaO and NaF. Most of the metallic fluorides (including silver fluoride) are soluble in water. [But, CaF_2 and SrF_2 are practically insoluble in water due to their high lattice energy.] Some metallic fluorides combine with hydrofluoric acid to form acid fluorides: $NaF+HF=NaHF_2$. Many double or complex fluorides like Na_3AlF_6, Na_3FeF_6 are also known and these are sparingly soluble in water. Due to its high electronegativity and small covalent radius, fluorine forms fluorides with many metals in their higher oxidation states, such as in CoF_3, AgF_2 *etc.*

Solvent action of liquid hydrofluoric acid : Anhydrous hydrofluoric acid is a highly associated liquid (b.p. = 19·5°C). It has high dielectric constant and dipole moment (comparable to those of water) and as such, it acts as a good ionizing solvent. Many metallic fluorides, fluroborates and perchlorates dissolve in liquid HF by producing anions like HF_2^-, BF_4^- and ClO_4^-. Alkali sulphates and periodates are also soluble in this solvent to some extent. Complex fluorides like Na_3AlF_6 dissolve in liquid HF to give ionic solutions. Some non-metallic fluorides like PF_5, AsF_5 and SbF_5 dissolve in it with the formation of PF_6^-, AsF_6^- and SbF_6^- ions respectively. Many inorganic salts, like alkali halides (other than fluorides) and cyanides dissolve in anhydrous HF and are decomposed thereby to form soluble metal fluorides and liberate hydrogen halides and HCN respectively :

$$MX+HF \rightleftharpoons M^+ + F^- + HX \text{ (X = Cl, Br, I, CN).}$$

Sulphuric acid dissolves in liquid HF to form fluosulphuric acid, H_3O^+ and F^-. Many organic compounds like alcohols, acids, ethers *etc.* dissolve in liquid HF to form conducting solutions. The solute molecule accepts the proton from HF to form the complex positive ion during the process of dissolution :

$ROH+HF \rightleftharpoons ROH_2^+ + F^-$; $R.COOH+HF \rightleftharpoons R.COOH_2^+ + F^-$; $R_2O+HF \rightleftharpoons R_2OH^+ + F^-$. Nitric acid dissolves in liquid HF by accepting a proton and thus behaves as a base in this highly acidic solvent (See, theories of acids and bases, Vol. I, Chapter V) :

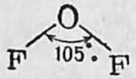
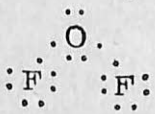
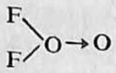
$$HNO_3 + HF \rightleftharpoons H_2NO_3^+ + F^-.$$

Tests : (i) Hydrofluoric acid may be detected by its etching action on glass. (ii) A mixture of fluoride and conc. H_2SO_4, on heating in a test tube, produces vapours which, on contact with a drop of water, forms gelatinous silicic acid. (iii) On adding $BaCl_2$ soln. to a soln. of a fluoride in water, a white ppt. of BaF_2 is formed. The ppt. is soluble in conc. HCl.

The quantitative estimation of fluoride is carried out by titrating a fluoride solution with standard thorium nitrate soln. with alizarin-S indicator, till a red colour or lake is formed.

Oxides of fluorine : Fluorine forms two oxides, *viz.* **fluorine monoxide (F_2O)** and **difluorine dioxide (F_2O_2).** These two oxides are not formed by the direct combination of the elements, even at elevated temperatures, but they are prepared by indirect methods. The best method of their preparation, together with their important properties and structures, are given in the following table :

Table 18·3 : The oxides of fluorine

Name and formula	Method of preparation	Important properties	Structure
1. Fluorine monoxide (F_2O) or, Oxygen difluoride (OF_2)	Prepared by the action of fluorine on dilute alkali solutions.	Colourless gas with strong smell. Fairly stable and a strong oxidising agent. Liberates I_2 from KI soln. : $F_2O + 4KI + H_2O = 2KF + 2KOH + 2I_2$.	 
2. Difluorine dioxide (F_2O_2) or, Oxygen monofluoride (O_2F_2)	Formed as an orange-red solid by the action of electric discharge on a mixture of O_2 and F_2 at low temperature and pressure.	Highly unstable ; decomposes into constituents at −100°C. Melts at −163·5°C.	

Abnormalities of fluorine : As the first member of the group, fluorine differs remarkably from other halogens, as is true for the first member in all other groups of the Periodic table. The abnormalities of fluorine, as compared with the other halogens, are ascribed to its extreme electronegative character, unit negative valency and fairly low atomic volume. In fact, fluorine tends to resemble the neighbouring element oxygen in the previous group in some of its properties. Some of the abnormalities of fluorine are enumerated below:

(i) Unlike the other halogens, fluorine cannot be prepared by heating a solid fluoride with MnO_2 and conc. H_2SO_4.

(ii) Fluorine is extremely reactive. With moist hydrogen, it combines with explosive violence even at $-252°C$.

(iii) Fluorine reacts with water to give ozonised oxygen even in the cold, while Cl_2 and Br_2 form hydrohalic and hypohalous acids and I_2 does not react.

(iv) With dilute alkali solutions, fluorine forms F_2O, while with conc. alkalis, only oxygen is liberated. Other halogens form hypohalites, halides and halates under different conditions.

(v) In the two known oxides of fluorine, the halogen is the negative component with -1 oxidation state. But, in the oxides of other halogens, these elements function as the positive component, sometimes with higher positive oxidation states.

(vi) Fluorine is a very strong oxidising agent and forms compounds with many metals and non-metals by bringing about their highest covalency, as in SiF_4, PF_5, SeF_6, SF_6, IF_7 *etc.* The highest fluorides of Co and Ag are CoF_3 and AgF_2, while the other halides of these two metals are CoX_2 and AgX (X=a halogen other than fluorine).

(vii) Unlike any other halogen, fluorine does not form any oxyacid.

(viii) The hydride of fluorine (HF) possesses some unique properties as compared to those of other halogen hydrides. Thus, HF is a strongly associated liquid (b. p.=19·5°C), while the other halogen hydrides are non-associated gaseous substances. So, HF is capable of giving rise to acid salts, *e.g.* KHF_2, which are not known for other halogens. Particularly interesting is the fact that, in combination with organic bases, HF acts as a tetrabasic acid, as in $R.NH_2.4HF$. Solubilites in water of some metallic fluorides are also radically different from those of the corresponding metallic salts of other hydrohalic acids. Thus, silver and mercurous fluorides, unilke other Ag^+ and Hg_2^{++} halides, are soluble in water, but CaF_2 and LiF are insoluble in water.

(ix) Fluorine differs from other halogens in that HF forms complex acids like fluoboric acid (HBF_4) and hydrofluosilicic acid (H_2SiF_6). Other hydrogen halides do not form such compounds.

(x) Aqueous solution of HF attacks glass, but solutions of other hydrogen halides do not.

(xi) Fluorine forms electrovalent compounds with Al and mercuric mercury. But, the other halides of these two metals are covalent compounds.

CHLORINE

Occurrence : Chlorine does not occur free in nature because of its high reactivity. But, in the combined state, it is fairly abundant. The most important source of chlorine is sodium chloride which occurs as common salt or rock-salt. Sea-water contains about 2–3% NaCl. The element also occurs in minerals like *sylvine* (KCl) and *carnallite* ($KCl.\ MgCl_2.\ 6H_2O$) in the Stassfurt deposits, and also as *horn silver* (AgCl).

Preparation : Chlorine is usually prepared in the laboratory by oxidising hydrochloric acid with manganese dioxide or potassium permanganate.

Powdered manganese dioxide or *pyrolusite* (naturally occurring MnO_2) is heated with conc. HCl in a round-bottomed flask, fitted with a thistle funnel and a delivery tube. A dark brown solution is first formed, which evolves chlorine on gentle heating. The evolved gas is washed with water, dried with conc. H_2SO_4 and collected by the upward displacement of air : $MnO_2+4HCl=MnCl_2+2H_2O+Cl_2\uparrow$.. [The brown solution produced at the beginning of the above reaction contains higher chlorides of manganese ($MnCl_4$ and/or $MnCl_3$), which decompose into $MnCl_2$ and Cl_2 on heating.] Conc. HCl in the above experiment may be replaced by a mixture of common salt and conc. H_2SO_4 : $4NaCl+MnO_2+4H_2SO_4=4NaHSO_4+MnCl_2+2H_2O+Cl_2\uparrow$.

The above reaction was earlier used for the manufacture of chlorine by the *Weldon Process*. From the mother-liquor containing $MnCl_2$, manganese was recovered by treatment with excess of milk of lime, when manganous hydroxide was precipitated : $MnCl_2 + Ca(OH)_2 = Mn(OH)_2 \downarrow + CaCl_2$. Air was then blown through the mixture at 60°C to oxidise $Mn(OH)_2$ to MnO_2. The latter combined with excess of lime to form calcium manganite, $CaO.MnO_2$ which, on addition of more manganous liquor and aeration, produced black calcium dipermanganite, $CaO.2MnO_2$, commonly known as *Weldon mud*. This was used in the decomposition of HCl again. The process is, however, obsolete now.

A continuous stream of chlorine gas may be obtained in the laboratory by dropping conc. HCl on powdered $KMnO_4$ in a flask. In this case, the evolution of Cl_2 takes place in the cold.

$$2KMnO_4 + 16HCl = 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2 \uparrow$$

Almost pure chlorine can be prepared by gently heating pure potassium dichromate with concentrated hydrochloric acid :

$$K_2Cr_2O_7 + 14HCl = 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2 \uparrow$$

Chlorine can also be detained by the action of dilute acids on bleaching powder :

$$Ca(OCl)Cl + 2HCl = CaCl_2 + H_2O + Cl_2 \uparrow .$$

The gas prepared by this method is often contaminated with CO_2, which is formed from $CaCO_3$ present in bleaching powder.

Hydrogen chloride gas can be oxidised to chlorine when its mixture with air is heated in presence of a copper salt as catalyst. This was the basis of the manufacture of chlorine by the *Deacon Process* which is, however, obsolete nowadays. In this process, a mixture of HCl gas and air was passed over heated (450°C) broken bricks, previously soaked in $CuCl_2$ solution and dried. The over-all reaction is represented as : $4HCl + O_2(air) \rightleftharpoons 2H_2O + 2Cl_2$. The reaction is reversible, effecting conversion of only two-thirds of the HCl used into chlorine. The mechanism of the catalytic reaction is represented as follows : $2CuCl_2 \rightleftharpoons 2CuCl + Cl_2 \uparrow$; $4CuCl + O_2 \rightleftharpoons 2(CuO.CuCl_2)$; $2(CuO.CuCl_2) + 4HCl \rightleftharpoons 4CuCl_2 + 2H_2O \uparrow$. It is seen that cupric chloride is .regenerated in the process, and the process is made continuous. The products, containing Cl_2, excess of HCl gas and nitrogen of air, were washed with water to recover unchanged HCl and then dried with conc. H_2SO_4. Chlorine obtained by this process contains nitrogen of the air used.

At present, chlorine is manufactured by electrolysing brine, or it is obtained on a large scale as a by-product in the electrolytic production of caustic soda or sodium carbonate (See Vol. I, Chapter XI). Chlorine is stored and transported in steel cylinders, after being liquefied by compression or cooling.

Properties : Chlorine is a greenish yellow, poisonous gas, with suffocating odour. It is about $2\frac{1}{2}$ times as heavy as air. It can be liquefied to an amber yellow liquid at 15°C by a pressure of 6 atmospheres, or only by cooling in a freezing mixture of solid carbon dioxide (*dry ice*) and ether.

Chlorine is chemically very active. Except carbon, nitrogen and oxygen, it combines directly with hydrogen and with most of the metallic and non-metallic elements. Hydrogen and chlorine combine with explosive violence, when their mixture is exposed to light. But, in presence of active charcoal, hydrogen and chlorine combine smoothly and rapidly in the dark to produce hydrogen chloride. A jet of either of the two gases also burns in the other to form HCl. [This reaction is used for the manufacture of HCl.] The high affinity of chlorine for hydrogen is also manifested by its power of removing hydrogen from hydrogen-containing substances. It, therefore, acts as an oxidising agent. Thus, a mixture of methane or ethylene (1 vol.) with chlorine (2 vols.) burns, when kindled, to form HCl, with the deposition of carbon (as soot). A piece of filter paper, soaked with warm turpentine ($C_{10}H_{16}$) bursts into flame with the deposition of black clouds of carbon and forming HCl :

$$CH_4+2Cl_2=C\downarrow+4HCl : C_2H_4+2Cl_2=2C\downarrow+4HCl ;$$
$$C_{10}H_{16}+8Cl_2=10C\downarrow+16HCl.$$

But, chlorine readily adds to the double bonds of ethylene to form ethylene dichloride : $C_2H_4+HCl_2=C_2H_4Cl_2$. A mixture of methane and Cl_2, on exposure to diffused sunlight, forms chlorinated hydrocarbons and HCl through substitution reactions :

$$CH_4+Cl_2=CH_3Cl+HCl ; CH_3Cl+Cl_2=CH_2Cl_2+HCl ;$$
$$CH_2Cl_2+Cl_2=CHCl_3+HCl ; CHCl_3+Cl_2=CCl_4+HCl.$$

Chlorine also acts as an oxidant by direct combination with other substances. For example, it oxidises ferrous chloride and stannous chloride to ferric chloride and stannic chlorides respectively : $2FeCl_2+Cl_2=2FeCl_3$; $SnCl_2+Cl_2=SnCl_4$. Chlorine oxidises ammonia to nitrogen ; but, if excess chlorine is used, a highly explosive liquid, nitrogen trichloride, is formed :

$$3Cl_2+8NH_3=6NH_4Cl+N_2 ; 3Cl_2+4NH_3=NCl_3+3NH_4Cl.$$

Chlorine combines directly with SO_2 and CO in sunlight or in presence of active charcoal, to form sulphuryl chloride and carbonyl chloride (phosgene) respectively :

$$SO_2+Cl_2=SO_2Cl_2 \;;\; CO+Cl_2=COCl_2.$$

Chlorine dissolves in water to an appreciable extent to form a yellow solution, commonly known as *chlorine water*, which possesses strong oxidising power. On passing Cl_2 into ice-cold water, pale greenish-yellow crystals of *chlorine hydrate*, $Cl_2.6H_2O$, are formed. Chlorine water bleaches litmus and other vegetable colouring matter. The oxidising and the bleaching properties of chlorine water are due to the production of *nascent* oxygen from water by chlorine : H_2O+ $+Cl_2=2HCl+[O]$. In chlorine water, an equilibrium is set up with the formation of hydrochloric and hypochlorous acid, which is, in fact, the hydrolysis of chlorine : $Cl_2+H_2O \rightleftharpoons HCl+HOCl$. In diffused sunlight, the solution of HOCl forms a mixture of hydrochloric and chloric acids as a result of self-oxidation and reduction : $3HOCl=HClO_3+2HCl$. Hypochlorous acid, however, breaks up into HCl and O_2 on exposure to bright sunlight : $2HOCl=2HCl+$ $O_2\uparrow$.

Chlorine water oxidises SO_2 to H_2SO_4, liberates sulphur from H_2S, bromine and iodine from solutions of bromides and iodides respectively : $SO_2+2H_2O+Cl_2=H_2SO_4+2HCl$; $H_2S+Cl_2=2HCl$ $+S\downarrow$; $2KBr+Cl_2=2KCl+Br_2$; $2KI+Cl_2=2KCl+I_2$.

Chlorine reacts with cold and dilute solutions of NaOH, KOH or $Ca(OH)_2$ to give chlorides and hypochlorites, so long the alkali remains in excess : $Cl_2+2NaOH=NaCl+NaOCl+H_2O$; $2Cl_2+$ $2Ca(OH)_2=CaCl_2+Ca(OCl)_2+2H_2O$. But, if chlorine is used in excess, the hypochlorite readily changes to chlorate. With hot and concentrated solutions of alkalis, however, chlorides and chlorates are formed : $3Cl_2+6NaOH$ (hot and conc.)$=5NaCl+NaClO_3+$ $3H_2O$; $6Ca(OH)_2$ (hot and conc.)$+6Cl_2=5CaCl_2+Ca(ClO_3)_2+$ $6H_2O$. Chlorine reacts with slaked lime at about 40°C to form bleaching powder : $Ca(OH)_2+Cl_2=Ca(OCl)Cl+H_2O$. When Cl_2 gas is passed over red-hot CaO, calcium chloride and oxygen are formed : $2CaO+Cl_2=2CaCl_2+O_2$.

Photochemical combination of H_2 and Cl_2 : Hydrogen and chlorine combine to form HCl on exposure to light (*photochemical reaction*). The reaction becomes violent except in the diffused light. It is assumed to be a *chain reaction*, in which the products of the primary reaction are re-generated in a subsequent stage to continue the chain indefinitely :

$$
\begin{aligned}
&Cl_2 + \text{light energy} \rightarrow 2Cl\,; \\
&Cl + H_2O \rightarrow HCl + H\,; \\
&H + Cl_2 \rightarrow HCl + Cl, \text{ and so on.}
\end{aligned}
$$

It may be seen from above that the chlorine atoms formed at the start from the dissociation of Cl_2 molecules by the absorption of light are regenerated at the third stage to continue the chain over and over again.

Uses : Chlorine is widely used for bleaching paper-pulp, cotton and linen textiles, either in the free state in solution or as a hypochlorite or bleaching powder. It is also used for sterilizing drinking water and for the preparation of metal chlorides and chlorates, sulphur chloride, carbonyl chloride, bleaching powder hydrochloric acid *etc.* It has also large application as a chlorinating agent for organic substances, for refining petroleum and for the production of intermediates of synthetic rubber.

COMPOUNDS OF CHLORINE

HYDROGEN CHLORIDE.

Preparation : Hydrogen chloride is prepared in the laboratory by heating sodium chloride with conc. H_2SO_4. The evolved gas is dried by passing through conc. H_2SO_2 or fused $CaCl_2$ and collected by upward displacement of air, or over mercury : $NaCl + H_2SO_4 = NaHSO_4 + HCl\uparrow$. [The gas cannot be dried by passing through P_2O_5, as it reacts with the desiccant : $2P_2O_5 + 3HCl = POCl_3 + 3HPO_3$] A steady supply of the gas may be obtained from a Kipp's apparatus by the action of conc. H_2SO_4 on lumps of NH_4Cl. Very pure HCl gas may be prepared by the hydrolysis of silicon tetrachloride : $SiCl_4 + 2H_2O = SiO_2 + 4HCl\uparrow$.

Hydrochloric acid is an aqueous solution of hydrogen chloride. The solution may be prepared by passing the HCl gas into water by means of an inverted funnel, or by inserting an empty glass-container in between the gas-supply and the absorbing vessel to avoid back-suction of water into the reaction-flask.

Hydrochloric acid is manufactured either as a by-product in the manufacture of salt cake (see p. 390 of volume I), or through synthesis from H_2 and Cl_2 obtained in certain electrolytic processes. Electrolytic chlorine is allowed to burn in electrolytic hydrogen in a large tank made of acid-resisting materials, and the product is dissolved in water. Synthesis of HCl may also be effected by passing a mixture of steam and chlorine over active charcoal as a catalyst :

$$2Cl_2+2H_2O=4HCl+O_2.$$

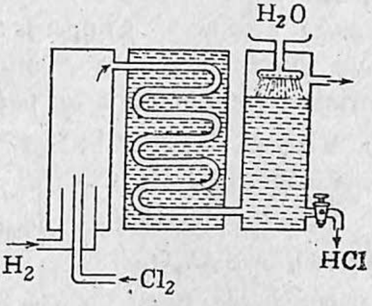


Fig. 18·3

Properties : Hydrogen chloride is a heavy, colourless gas with a pungent smell. The gas neither burns nor supports combustion ; but, a piece of burning sodium continues to burn in it to form NaCl and hydrogen : $2Na+2HCl=2NaCl+H_2$. It can be liquefied by cooling with liquid air to a colourless, non-conducting liquid. The liquid and its vapour evidently consist of covalent molecules. The dry liquid exhibits no acid property. Thus, it has no action on metals like Zn, Fe and Mn or on compounds like CaO and some carbonates. But, peculiarly enough, aluminium dissolves in it with the evolution of hydrogen. Tin and iron are converted into $SnCl_2$ and $FeCl_2$, with the liberation of hydrogen, when the metals are heated in a current of gaseous hydrogen chloride : $Sn+2HCl=SnCl_2+H_2$; $Fe+2HCl=FeCl_2+H_2$.

Gaseous hydrogen chloride is highly soluble in water. The dissolution takes place with considerable evolution of heat, giving a strongly acid solution, usually known as hydrochloric acid. A saturated aqueous solution contains 42% hydrogen chloride dissolved in it. But, on distilling a solution of HCl in water, a constant-boiling liquid, boiling at 110°C, distils over, and this contains about 20·2% HCl. The aqueous solution of HCl is a good conductor of electricity and behaves as a strong monobasic acid. The covalent molecule of gaseous HCl dissociates extensively in aqueous solution to produce H^+ and Cl^- ions. Hydrochloric acid dissolves basic oxides, liberates CO_2 from carbonates and neutralises alkalis. The dilute acid dissolves metals like zinc, iron and magnesium with the liberation of hydrogen ; tin and aluminium dissolve in the hot and concentrated acid. Copper is slowly attacked by the concentrated acid, forming cuprous chloride which dissolves readily with the formation of complex acids like $H[CuCl_2]$ and $H_2[CuCl_3]$:

$$2Cu+2HCl=2CuCl+H_2\uparrow \; ; \; CuCl+HCl=H[CuCl_2] \; ;$$
$$CuCl+2HCl=H_2[CuCl_3].$$

The acid is readily oxidised by oxidising agents like MnO_2, $KMnO_4$ or $K_2Cr_2O_7$.

Composition of HCl : The volumetric composition of HCl can be ascertained by (i) the analytical method, or (ii) the synthetic method.

(i) **The analytical method.**—A concentrated solution of hydrochloric acid (sp.gr.=1·1) is electrolysed with carbon electrodes in a two-limbed glass voltameter (Fig. 18·4). Hydrogen is liberated at the cathode and chlorine at the anode (after the anodic solution is saturated with chlorine). If the gases are collected and their volumes measured after the saturation of the anodic solution with chlorine, it will be found that equal volumes of the two gases are collected at the two limbs of the voltameter. It is concluded from the results of this experiment that *hydrogen chloride contains equal volumes of hydrogen and chlorine*. But, these results do not give any idea about how much volume of hydrogen chloride has produced the noted volumes of H_2 and Cl_2. So, the molecular formula of hydrogen chloride cannot be deduced from these results. The following experiment should, therefore, supplement the above to find out the molecular formula of hydrogen chloride by the analytical method :

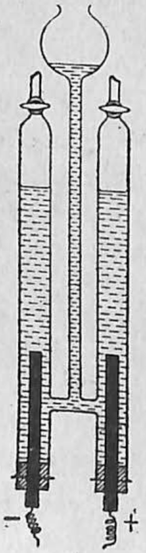


Fig. 18·4

Moist sodium amalgam is introduced into a known volume of hydrogen chloride collected over mercury in the stoppered limb of the apparatus shown in fig. 18·5. Sodium amalgam reacts with HCl to form NaCl (which occupies practically little volume) and H_2. It is found after the completion of the reaction that the volume of H_2 that remains is equal to half the volume of HCl gas taken. The results show that *hydrogen chloride contains half its volume of hydrogen.*

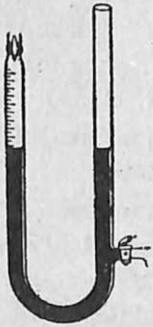


Fig. 18·5

It has been found from the first experiment that hydrogen chloride contains equal volumes of H_2 and Cl_2. So, combining the results of the two experiments, we can say that,

2 vols. of hydrogen chloride contain 1 vol. of hydrogen and 1 vol. of chlorine
or, 2 mols. ,, ,, ,, 1 mol. ,, ,, 1 mol. ,,
or, 2 mols. ,, ,, ,, 2 atoms ,, ,, 2 atoms ,,
or, 1 mol. ,, ,, ,, 1 atom ,, ,, 1 atom ,,

So, the molecular formula of hydrogen chloride is HCl, which is also confirmed by its molecular weight (36·5), as determined from the vapour density measurement.

(ii) **The synthetic method.**—Equal volumes of H_2 and Cl_2 are collected separately in the two bulbs (of equal capacity) of a glass apparatus (Fig. 18·6). Each of the two bulbs is provided with a stop-cock at one end and they are connected by a narrow glass-tuble which is also provided with a stop-cock. The two gases are allowed to mix together by opening the middle stop-cock and the apparatus is kept in diffused daylight for about 48 hours, so that the combination between hydrogen and chlorine to form hydrogen chloride is complete. [This is indicated by the disappearance of the greenish colour of chlorine.] After the completion of the reaction, one of the ends of the apparatus is dipped in a trough of mercury and the end stop-cock is opened. No gas comes out of the apparatus and mercury also does not enter the apparatus. This shows that there is no change in volume of the gases when H_2 and Cl_2 are combined. But, on opening one end of the apparatus under water, it is seen that the apparatus is completely filled up, as water rushes in by dissolving the hydrogen chloride. This proves that, *one volume of hydrogen combines with one volume of chlorine to produce two volumes of hydrogen chloride.* So, by applying Avogadro's law to the results of the experiment, it comes out that, 1 molecule of hydrogen chloride contains $\frac{1}{2}$ molecule or 1 atom of hydrogen and $\frac{1}{2}$ molecule or 1 atom of chlorine. Hence, the molecular formula of hydrogen chloride is HCl, which is confirmed from the molecular weight as determined by its vapour density measurement.

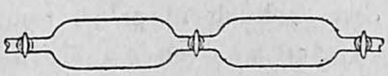


Fig. 18·6

Uses : Hydrochloric acid has many applications in various industries. It is used in dyeing and textile printing ; for pickling iron sheets before tinning, galvanising or enamelling ; for manufacturing glue and glucose ; for preparing metallic chlorides etc. It also finds important applications as a reagent and an acid in chemical laboratories. Aqua-regia is prepared from it. It is also used in medicine.

Tests : (i) A soln. of HCl or chloride produces a curdy white ppt. on treatment with $AgNO_3$ soln. The ppt. is insoluble in HNO_3, but soluble in NH_4OH. (ii) A conc. soln. of HCl or a mixture of a solid chloride and conc. H_2SO_4, when heated with MnO_2, evolves a greenish yellow gas (chlorine) with irritating smell. The gas turns a moist starch-iodide paper blue.

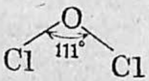
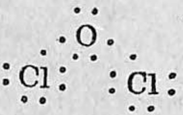
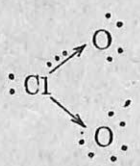
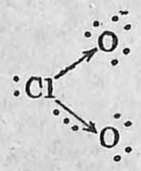
Hydrochloric acid or a chloride is estimated by precipitating from a soln. as AgCl in presence of HNO_3 and weighing the dried ppt. It can also be estimated by titrating with a standard soln. of $AgNO_3$, using potassium chromate indicator.

Oxides of Chlorine.

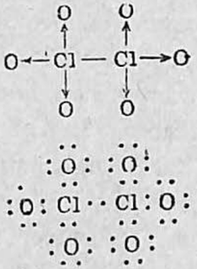
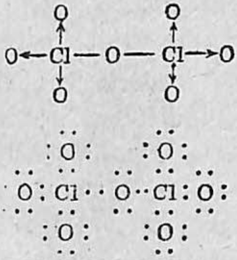
There are four well-characterised oxides of chlorine. They are generally prepared by indirect methods. These are : (i) **Chlorine monoxide (Cl_2O)**, (ii) **Chlorine dioxide (ClO_2)**, (iii) **Chlorine hexoxide (Cl_2O_6)** and (iv) **Chlorine heptoxide (Cl_2O_7)**. Their best methods of preparation, state of aggregation and accepted structure are given in Table 18·4 :

TABLE 18·4

Oxides of Chlorine

Name and formula	Best method of preparation	State of aggregation and important property	Structure
Chlorine monoxide (Cl_2O)	Obtained by passing Cl_2 over precipitated HgO, previously heated to 300°C : $2Cl_2+2HgO$ $=HgO.HgCl_2$ $+Cl_2O\uparrow$.	Brownish yellow gas ; condenses to an orange liquid (b. p. 2°C) on cooling. Disssolves in water to give a soln. of hypochlorus acid : $Cl_2O+H_2O=2HOCl$.	 
Chlorine dioxide (ClO_2)	Prepared by passing dry Cl_2 over silver chlorate at 90°C : $2AgClO_3+Cl_2=$ $2AgCl+2ClO_2+O_2$.	Yellow gas ; condenses to a dark-red liquid (b.p. 11°C) and freezes to orange crystals at −59°C. Aqueous soln. is neutral ; but reacts with bases to give chlorites and chlorates : $2ClO_2+2KOH=KClO_3$ $+KClO_2+H_2O$.	 

Continued

Name and formula	Best method of preparation	State of aggregation and important property	Structure
Chlorine hexoxide (Cl_2O_6)	Obtained by the action of ozonized oxygen on ClO_2 at 0°C, and by fractionating the products : $2ClO_2+2O_3 = Cl_2O_6+2O_2$.	Dark-red unstable liquid, freezing at 3·5°C. Reacts with alkalis to give chlorates and perchlorates : $Cl_2O_6+2KOH=KClO_3 +KClO_4+H_2O$.	
Chlorine heptoxide (Cl_2O_7)	$HClO_4$ is added to P_2O_5 at −10°C. The mixture is kept for 24 hours add then distilled at 85°C : $2HClO_4+P_2O_5 =Cl_2O_7\uparrow +2HPO_3$.	An oily, colourless liquid (b.p. 82°C). Reacts with water to give perchloric acid : $Cl_2O_7+H_2O =2HClO_4$.	

The isolation of chlorine tetroxide (ClO$_4$) through the reaction, $2AgClO_4+I_2 =2AgI+2ClO_4$, has been claimed. But, there appears to be much controversy among the chemists about this oxide. It is often believed that the substance is a free radical which may exist in the dimeric form, $(ClO_4)_2$. It reacts with water and metals to produce perchloric acid and metal perchlorates respectively.

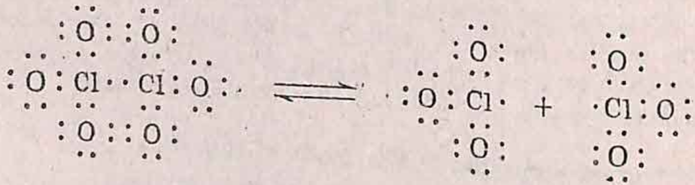
Other important properties of the oxides of chlorine :

Chlorine monoxide (Cl_2O) : The gas is thermally unstable and explodes on heating or in the presence of reducing agents, into chlorine and oxygen : $2Cl_2O=2Cl_2+O_2$. It is an oxidising agent and oxidises sulphur to SO_2, phosphorus to P_2O_5 and even hydrogen chloride to chlorine. It is the anhydride of hypochlorous acid (HOCl) which is formed on dissolving the gas in water. With alkalis, it forms hypochlorites : $Cl_2O+2KOH=2KOCl+H_2O$.

The structure of Cl_2O is angular as shown in the Table 18·4, the Cl—O bond distance being 1·71 Å and the Cl—O—Cl bond angle being 111°.

Chlorine dioxide (ClO_2) : It readily explodes on heating, or in contact with hot glass, or when sparked. Explosion also takes place when the oxide comes in contact with organic substances like alcohol, ether, turpentine oil *etc.* It is a powerful oxidising agent and liberates iodine from acidified KI solution : $10\,KI+8HCl+2ClO_2=10KCl+4H_2O+5I_2$. The compound is paramagnetic and contains an odd number of electrons. Its structure is shown in the Table. It is angular with the O—Cl—O angle of 117°. The Cl—O bond lengths are appreciably shorter than in a single bond, and it is believed that resonance occurs between the two structures shown, each of which involves two co-ordinate bond and a three-electron bond occupying either position [See also Vol. I, p. 144]. It is often considered as the mixed anhydride of chlorous and chloric acids.

Chlorine hexoxide (Cl_2O_6) : This oxide also explodes on heating, though less violently than ClO_2. It dissolves unchanged in water, but produces chlorates and perchlorates with alkalis, as already stated. It is, therefore, often considered as the mixed anhydride of chloric and perchloric acids. It is a strong oxidant. The compound contains no unpaired electrons and hence, should be diamagnetic. But, in the liquid state and in aqueous solution, it exhibits paramagnetism. So, it is probable that it undergoes dissociation into odd molecules ClO_3, with an unpaired electron on the chlorine atom : $Cl_2O_6 \rightleftharpoons 2ClO_3$.



Cl_2O_6 (Diamagnetic) ClO_3 (Paramagnetic)

Fig. 18·7

Chlorine heptoxide (Cl_2O_7) : It is a moderately stable oxide of chlorine and is the anhydride of perchloric acid. It is a mild oxidising agent and forms perchloric acid and perchlorates on reaction with water or bases (or metals). The accepted structure of the compound is shown in the Table. Studies of the Raman spectra of the compound shows that two ClO_3 groups are bridged by an oxygen atom, the Cl-O-Cl angle being 128°

Oxyacids of Chlorine : Chlorine has four well-known oxyacids. These are :

Hypochlorous acid, HOCl ;
Chlorous acid, $HClO_2$;
Chloric acid, $HClO_3$;
Perchloric acid. $HClO_4$;

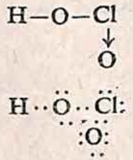
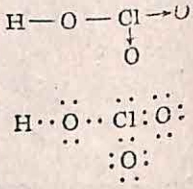
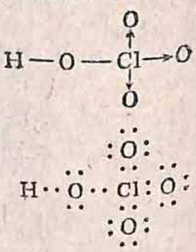
As already stated, the strength and stability of the oxyacids of chlorine increase with the number of oxygen atoms in the molecule. Thermal stability of the oxyacids also increase with the molecular weight. The best methods of the preparation of the oxyacids of chlorine, together with their important properties and the accepted structures are given in the Table 18·5 :

TABLE 18·5

The Oxyacids of Chlorine

Name and formula	Method of preparation	Important properties	Accepted structure
Hypochlorous acid (HOCl)	An aqueous solution (~ 25%) is prepared by shaking precipitated HgO with chlorine water and then distilling the filtered solution : $2HgO+2Cl_2+H_2O =2HOCl+HgCl_2.HgO$. May also be prepared by passing a stream of CO_2 into a suspension of bleaching powder in water : $2Ca(OCl)Cl+H_2O+CO_2=CaCl_2+CaCO_3\downarrow +2HOCl$.	The soln. of the acid is pale yellow in colour, with a pleasant smell. It is a very weak acid, stable when kept cool in the dark. Decomposes by heat or on exposure to light, evolving Cl_2 and O_2, with the formation of some chloric acid : $2\,HOCl=2HCl+O_2$; $HCl+HOCl=H_2O+Cl_2$; $3HOCl=HClO_3+2HCl$. It reacts with alkalis to form hypochlorites : $NaOH+HOCl \rightleftharpoons NaOCl+H_2O$.	H–O–Cl $H\cdot\cdot\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}\cdot\cdot\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:$

Continued

Name and formula	Method of preparation	Important properties	Accepted structure
Chlorous acid ($HClO_2$)	An aqueous soln. of the acid is prepared by the action of dil. H_2SO_4 on barium chlorite and filtering off the precipitated barium sulphate: $Ba(ClO_2)_2+H_2SO_4= BaSO_4\downarrow+2HClO_2$. [Barium chlorite is prepared by the reaction of ClO_2 with a suspension of BaO_2 in H_2O_2: $2ClO_2+H_2O_2=2HClO_2 +O_2$; $BaO_2+2HClO_2 =Ba(ClO_2)_2+H_2O_2$.]	It is a moderately weak acid, the K_a being 10^{-2}. The weak acid soln. is unstable and decomposes rapidly: $4HClO_2=2ClO_2+ClO_3^- +Cl^-+2H^++H_2O$.	 $\mathrm{H-O-\underset{\underset{O}{\downarrow}}{Cl}}$
Chloric acid ($HClO_3$)	Obtained as a 40% soln. by treating barium chlorate soln. with dil. H_2SO_4 and evaporating the filtered soln. in a vacuum desiccator over conc. H_2SO_4: $Ba(ClO_3)_2+H_2SO_4 =BaSO_4\downarrow+2HClO_3$. Further concentration decomposes the acid: $3HClO_3=HClO_4+Cl_2\uparrow +2O_2\uparrow+H_2O$.	Colourless solution, with a pungent smell. Stable in the dark, but decomposes on exposure to light. It is a powerful oxidising and bleaching agent. Dissolves metals like Zn, Al and Fe, with the evolution of hydrogen.	 $\mathrm{H-O-\underset{\underset{O}{\downarrow}}{Cl}\rightarrow O}$
Perchloric acid ($HClO_4$)	Prepared by distilling potassium perchlorate with conc. H_2SO_4 at 10–20 mm. pressure, and blowing air through the distillate to remove HCl and CO_2. $KClO_4+H_2SO_4= KHSO_4+HClO_4$.	The anhydrous acid is a fuming, colourless mobile liquid; it boils at 90°C and explodes violently above 92°C. It is a strong oxidising agent and inflames organic substances like paper, wood *etc*. It is highly hygroscopic and dissolves in water with evolution of heat. The aqueous soln. has little oxidising power and dissolves many metals: $Zn+2HClO_4=Zn(ClO_4)_2 +H_2\uparrow$.	 $\mathrm{H-O-\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{Cl}}\rightarrow O}$

Other important properties of the oxyacids of chlorine.

Hypochlorous acid (HOCl) : As already stated, hypochlorous acid is a very weak acid, with $Ka = 3{\cdot}7 \times 10^{-8}$ at 18°C. It acts both as an oxidising agent and a bleaching agent, both these activities being due to the ease with which it produces nascent oxygen during the decomposition, $HOCl \rightleftharpoons HCl + O$. Hence, for the same weight of chlorine, it possesses twice the oxidising capacity of free chlorine. It liberates iodine from potassium iodide solution and oxidises manganous salts to MnO_2. The solution of the acid dissolves magnesium metal with the liberation of hydrogen.

Chlorous acid ($HClO_2$) : It is already stated that the pure acid cannot be isolated in the free state, but its aqueous solution (although not also very stable) can be prepared.

Chloric acid ($HClO_2$) : Chloric acid oxidises HCl and SO_2 to Cl_2 and H_2SO_4 respectively : $8HClO_3 + 16HCl = 6ClO_2 + 9Cl_2 + 12H_2O$; $3SO_2 \quad HClO_3 + 3H_2O = 3H_2SO_4 + HCl$. Organic matters like paper, wool *etc.* catch fire in contact with conc. $HClO_3$.

Perchloric acid ($HClO_4$) : The aqueous solution of perchloric acid behaves as the strongest acid known, with $Ka > 10^8$, and forms a constant-boiling mixture (b.p. 203°C) containing 71·6% of the acid. The acid also forms a stable solid monohydrate, $HClO_4.H_2O$, which melts at 50°C. In aqueous solution, the acid is reduced by sodium hydrosulphite, $Na_2S_2O_4$, alkaline ferrous hydroxide and by solutions of titannous salts.

HYPOCHLORITES, CHLORITES, CHLORATES AND PERCHLORATES.

Hypochlorites : These are the metallic salts of hypochlorous acid. Among these, sodium hypochlorite and bleaching powder are of much technical importance. Bleaching powder has been discussed in details in vol. I (chapter XIII) of this book.

Sodium hypochlorite (NaOCl) is formed when Cl_2 gas is passed into a dilute solution of NaOH in the cold : $2NaOH + Cl_2 = NaOCl + NaCl + H_2O$. Solutions of sodium hypochlorite are, however, prepared on a manufacturing scale by electrolysing a solution of NaCl in the cold in an unpartitioned cell, with platinum anode and iron cathode, when the discharged chlorine reacts with NaOH solution to form sodium hypochlorite and sodium chloride.

Pure sodium hypochlorite (free from NaCl) may be prepared by neutralising the free HOCl with NaOH solution. Very deliquesecnt crystals of $NaOCl.6H_2O$ may be isolated by cooling a concentrated solution of the substance.

Hypochlorites also possess the oxidising and the bleaching properties of hypochlorous acid. Being salts of a very weak acid, they are extensively hydrolysed in aqueous solution and are decomposed even by CO_2. Concentrated acids decompose them with the liberation of chlorine and oxygen : $4NaOCl+2H_2SO_4=2Na_2SO_4+2H_2O+O_2+2Cl_2$. They liberate iodine from KI solution, oxidise manganous salts to hydrated manganese dioxide ($MnO_2.2H_2O$), chromic salts to chromates and Pb(II) salts to PbO_2. Hydrogen peroxide is decomposed by them with the liberation of oxygen : $NaOCl+H_2O_2=NaCl+H_2O+O_2$.

Distinction between HOCl and Cl_2 : Free HOCl can be distinguished from Cl_2 by their reactions with metallic mercury. Hypochlorous acid forms brownish yellow basic mercuric chloride on shaking with mercury, the product being soluble in HCl : $Hg+HOCl=Hg(OH)Cl$. But, chlorine-water, on similar treatment with mercury, forms mercurous chloride (white) which is insoluble in HCl : $2Hg+Cl_2=Hg_2Cl_2$.

Chlorites : These are salts of chlorous acid. They are powerful oxidising agents. Alkali chlorites, especially sodium chlorite ($NaClO_2.3H_2O$; *Textone*), are used as an excellent bleaching agent for cellulose materials. Heavy metal chlorites, like those of silver and lead, explode on heating and as such, they were tried for use as detonators. But, they were found unsuitable for this purpose due to their unpredictable performance.

Chlorites are relatively stable in alkaline solution, but they decompose in acidic solutions. They liberate iodine from potassium iodide : $NaClO_2+4KI+2H_2O=NaCl+4KOH+2I_2$.

Chlorates : These are metallic salts of chloric acid, of which sodium chlorate ($NaClO_3$) and potassium chlorate ($KClO_3$) are the two most important members. It has earlier been stated that chlorate is formed, along with chloride, on passing Cl_2 gas into a hot and concentrated solution of caustic alkalis.

Sodium chlorate is prepared on a large scale by electrolysing a saturated aqueous solution of NaCl at 70°C in an undivided cell with iron cathodes and graphite anodes. The electrodes are placed closed together inside the cell, so that the products of electrolysis may come in contact with each other. [Some sodium dichromate is added to the electrolytic bath to prevent reduction of the chlorate by hydrogen.] The chlorine liberated at the anode reacts with the hydroxyl ions formed at the cathode, and hypochlorite and chloride are formed so long the liquid remains alkaline : $Cl_2+OH^-=OCl^-+Cl^-+H_2O$. When all the alkali in the bath is exhausted, free hypochlorous acid is formed, which reacts with hypochlorite ion to oxidise it to chlorate ion : $ClO^-+HOCl=ClO_3^-+2Cl^-+2H^+$. The total reaction may be represented as : $3Cl_2+6OH^-=ClO_3^-+5Cl^-+3H_2O$.

After the completion of the electrolysis, the solution of the cell is concentrated, when the less soluble NaCl crystallise out. It is filtered off and the filtrate, on further evaporation, yields crystals of sodium chlorate.

Sodium chlorate may also be prepared through the double decomposition between calcium chlorate and sodium sulphate. [Calcium chlorate is first obtained by saturating hot milk of lime with chlorine (see page 253 of this volume). Calcium chloride in the products is removed by concentrating and cooling the mixture, when $CaCl_2.6H_2O$ crystals separate out and are removed.] Calcium chlorate solution is usually mixed with some chloride, and excess of Na_2SO_4 solution is added. The precipitated $CaSO_4$ is filtered off and the filtrate evaporated, when the less soluble NaCl crystallise out and is removed. On cooling the filtrate, $NaClO_3$ crystals are obtained.

Sodium chlorate forms white crystals. Its properties are similar to those of potassium chlorate, described later. It is used as a weed-killer and for the preparation of potassium chlorate.

Potassium chlorate is prepared by mixing concentrated solutions of sodium chlorate and potassium chloride, when sparingly soluble $KClO_3$ separates out immediately : $NaClO_3+KCl=KClO_3+NaCl$.

Potassium chlorate is also obtained by treating a warm solution of calcium chlorate with solid potassium chloride, and cooling the mixture, when $KClO_3$ crytallises out.

Potassium chlorate is a white crystalline solid (mp. 370°C), sparingly soluble in cold water but readily so in hot water. On heating above its melting point, the salt decomposes into potassium chloride and potassium perchlorate : $4KClO_3=KCl+3KClO_4$. On further heating, oxygen is evolved and KCl is left as residue. But, when $KClO_3$ is mixed with MnO_2 and heated, it decomposes into KCl and O_2 below its melting point : $2KClO_3 = 2KCl + 3O_2$. Potassium chlorate is a strong oxidising agent. When warmed with conc. HCl, it produces a mixture of Cl_2 and ClO_2 (*euchlorine*) : $24HCl + 8KClO_3 = 8KCl + 12H_2O + 9Cl_2 + 6ClO_2$. On warming with conc. H_2SO_4, potassium chlorate evolves chlorine dioxide, with the formation of perchloric acid : $3KClO_3 + 3H_2SO_6 = 3KHSO_4 + HClO_4 + 2ClO_2 + H_2O$. It oxidises SO_2 to sulphuric acid : $KClO_3 + 3SO_2 + 3H_2O = KCl + 3H_2SO_4$. The solid salt forms explosive mixture with charcoal, sulphur or phosphorus.

Potassium chlorate is used in the manufacture of matches, fireworks and other explosives. It is also used for the preparation of oxygen and potassium perchlorate.

Perchlorates : These are the metallic salts of perchloric acid. Potassium perchlorate ($KClO_4$), sodium perchlorate ($NaClO_4$) and magnesium perchlorate [$Mg(ClO_4)_2$] are the most important salts of perchloric acid.

Potassinm perchlorate is obtained by the thermal decomposition of $KClO_3$ above its melting point : $4KClO_3 = KClO_4 + 3KCl$. The melt is cooled and leached repeatedly with cold water to remove KCl. The residue is then recrystallized from hot water.

Potassium perchlorate may also be prepared by the double decomposition between sodium perchlorate and potassium chloride solutions, when the sparingly soluble $KClO_4$ separates out.

Potassium perchlorate is very sparingly soluble in water and still less so in alcohol, so that potassium is often estimated gravimetrically as $KClO_4$. It is used in the preparation of fireworks or other explosives.

Sodium perchlorate is obtained by the electrolysis of a strong solution of $NaClO_3$ at 10°C, using iron cathodes and smooth platinum anodes. The salt is highly soluble in water.

Magnessium perchlorate has been discussed in details in Vol. I, Chapter XIII of this book.

BROMINE

Occurrence : Although bromine is not a very common element, it occurs in nature, mainly as the bromides of alkali metals (Na and K), calcium and magnesium, in some abundance. These bromides occur in sea-water in an average quantity of 0·065%. Certain dried up lakes in Africa and the U.S.A. (Dead Sea at Tunisia and Utah Salt Lake in America) are rich sources of these bromides. Stassfurt salt deposits also contain certain percentages of bromides.

Preparation : In the laboratory, bromine is prepared by cautiously distilling a mixture of potassium bromide and MnO_2 with conc. $H_2SO_4(40\%)$: $2KBr+MnO_2+3H_2SO_4=2KHSO_4+MnSO_4+Br_2+2H_2O$. The product is purified by distillation over solid KBr (to remove traces of Cl_2) and then treated with quicklime and anhydrous calcium bromide to dry and free it from traces of H_2SO_4 and HBr.

Bromine is manufactured from *bittern* or from sea-water.

(i) **From bittern :** Bittern is the residual liquid (*mother liquor*) left after the crystallisation of NaCl, KCl (and $MgCl_2$) from Dead Sea water and Stassfurt salts. The hot mother-liquor, containing $MgBr_2$ (and some $MgCl_2$) is allowed to trickle down a tower, provided with perforated shelves and packed with broken pieces of porcelain (Fig. 18·8). Within the tower, the percolating bittern meets with current of Cl_2 gas and steam which is pumped upwards from the bottom. Bromine is liberated from the bromides by chlorine and is swept out of the tower by steam

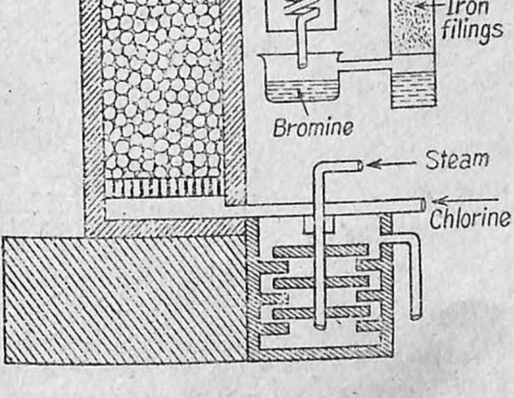


Fig. 18·8

through an outlet near the top and is condensed through the earthenware condensers. It is collected as a liquid in the receiver.

(ii) **From Sea-water :** In the U.S.A., bromine is extracted directly from sea-water. For this purpose, sea-water is acidified with H_2SO_4 and treated with chlorine. The liberated bromine is vaporised by blowing hot air, and the vapours are absorbed in NaOH or Na_2CO_3 solution, when a mixture of bromide and bromate of sodium is formed : $3Br_2+3Na_2CO_3=NaBrO_3+5NaBr+3CO_2\uparrow$. The mixture of bromide and bromate liberates bromine on acidification : $NaBrO_3+5NaBr+3H_2SO_4=3Na_2SO_4+3H_2O+3Br_2$. Bromine, thus produced, is purified by distillation.

Properties : Bromine is a volatile, dark-red, heavy liquid (b.p. 59°C). It has a disagreeable smell and is poisonous. (The vapours of bromine violently attack the mucous membrane and the liquid heavily corrodes the skins). It dissolves in water to some extent (36% at 20°C) to give a stable reddish-brown solution (bromide-water). A saturated solution of bromine in water deposits red crystals of bromine hydrate, $Br_2.10H_2O$, when cooled in a freezing mixture. It also dissolves in many organic solvents like alcohol, ether, chloroform, carbon disulphide *etc.* In its chemical properties, bromine resembles chlorine, but it is less reactive than the latter. It combines with hydrogen above 300°C to form hydrogen bromide which dissociates about 1% at 1200°C : $H_2+Br_2 \rightleftharpoons 2HBr$. Reactions of bromine with alkalis are analogous to those of chlorine, and the products obtained in these reactions are alkali hypobromites, bromates and bromides. Bromine displaces iodine from iodide solutions, sulphur from hydrogen sulphide and nitrogen from ammonia. It oxidises SO_2 to H_2SO_4, and H_3AsO_3 to H_3AsO_4. Liquid bromine combines vigorously with phosphorus, arsenic, potassium and many other metals. It bleaches moist litmus paper. It adds to the double bond of ethylenic compounds to form dibromo-derivatives : $C_2H_4+Br_2-C_2H_4Br_2$.

Uses : Bromine is used for making tear gases, methyl bromide (for fire extinguishers), ethylene dibromide (for use in petrol as an anti-knock agent), as a disinfectant and in medicine. It also finds application in the laboratories for brominating organic compounds and as an oxidising agent.

Tests : Bromine is detected by its red colour and irritating smell. It dissolves in chloroform or carbon disulphide to give a reddish brown soln. It turns starch-iodide paper blue and a starch soln. yellow.

COMPOUNDS OF BROMINE

Hydrogen bromide.

Preparation : Hydrogen bromide is prepared in the laboratory by the dropwise addition of liquid bromine from a dropping funnel on a mixture of red phosphorus and water kept in a round-bottomed flask. Phosphorus bromides (PBr_3 and PBr_5) are first formed, which are immediately hydrolysed by the water present into hydrogen bromide and the oxyacids of phosphorus :

$$2P+3Br_2=2PBr_3\ ;\ PBr_3+3H_2O=3HBr+H_3PO_3.$$

$$2P+5Br_2=2PBr_5\ ;\ PBr_5+4H_2O=5HBr+H_3PO_4.$$

The gaseous hydrogen bromide leaves the reaction-vsssel through the delivery pipe and then passes through two U-tubes (A) and (B),

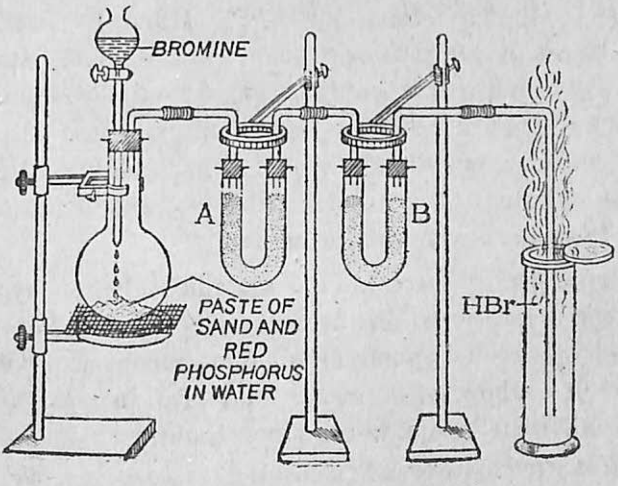


Fig. 18·9.—Preparation of HBr in the laboratory

containing moist red phosphorus and glass beads (to absorb bromine vapours) and anhydrous $CaBr_2$ (for drying the gas) respectively. The dried gas is collected over mercury. An aqueous solution of hydrogen bromide (hydrobromic acid) is prepared by passing HBr gas into water in a similar manner as described for the preparation of HCl solution.

Hydrogen bromide cannot be prepared by heating KBr with conc. H_2SO_4 due to the fact that the conc. acid oxidises HBr to bromine on heating: $KBr+H_2SO_4=KHSO_4+HBr$; $2HBr+H_2SO_4=Br_2\uparrow+SO_2\uparrow+2H_2O$.

Hydrogen bromide is prepared on a large scale by the action of bromine on benzene in presence of aluminium or iron powder as catalyst : $C_6H_6+Br_2=C_6H_5Br+HBr\uparrow$

An aqueous solution of hydrogen bromide can be readily obtained by passing a stream of SO_2 into bromine-water (liquid bromine covered with about 6 times its volume of water), till the whole solution attains a pale yellow colour. The solution is distilled and the distillate re-distilled over barium bromide to remove traces of H_2SO_4 formed : $Br_2+2H_2O+SO_2=H_2SO_4+2HBr$.

Properties : Hydrogen bromide is a colourless gas with irritating smell. It is heavier than air and highly soluble in water. The aqueous solution (Hydrobromic acid) forms a constant boiling mixture (b.p. 126°C) containing 47·6% HBr. Its properties are similar to those of hydrochloric acid ; but, it is less stable. The aqueous solution is quite easily oxidised and decomposed by air in presence of light : $4HBr+O_2=2H_2O+2Br_2$. It is also oxidised not only by manganese dioxide or permanganates, but also by conc. H_2SO_4 and chlorine. It is a quite strong acid and reacts with many metals and bases to form salts (bromides).

Metal bromides : These are the metallic salts of hydrobromic acid and are prepared by dissolving metals like Zn, Fe *etc.* in the aqueous acid, or by the interaction of the aqueous acid with oxides, hydroxides or carbonates of metals, and also, in certain cases, by heating the powdered metal in bromine vapour.

Uses : Hydrobromic acid is used for preparing bromides. It is also used as a reagent. KBr is used in medicine, while AgBr is used in photography.

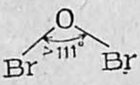
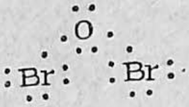
Tests : Hydrobromic acid or a bromide liberates bromine by the action of chlorine. The evolved bromine may be extracted in CS_2 to give a reddish yellow soln. When heated with conc. H_2SO_4, hydrobromic acid or a bromide is oxidised to form bromine vapours. An aqueous soln. of HBr or a bromide forms a light yellow ppt. of AgBr on treatment with $AgNO_3$ soln. The ppt. is insoluble in dil. HNO_3, but slowly dissolves in conc. NH_4OH soln.

Oxides of bromine.

Bromine forms three oxides. These are : (i) bromine monoxide (Br_2O), (ii) bromine dioxide (BrO_2) and (iii) bromine peroxide (BrO_3). Their best method of preparation, important properties and the accepted structures are given in Table 18·6 :

TABLE 18·6

Oxides of Bromine

Name and formula	Method of preparation	Properties	Structure
Bromine monoxide (Br_2O)	Obtained in small amounts by passing bromine vapours over mercuric oxide heated at 50–60°C : $HgO+2Br_2=HgBr_2+Br_2O$.	It is an unstable compound which readily decomposes into Br_2 and O_2 at room temperature, but is stable as a brown solid at $-40°C$. Dissolves in water to form unstable hypobromous acid : $Br_2O+H_2O=2HOBr$.	 
Bromine dioxide (BrO_2)	It is formed as a yellow solid by the action of electric discharge on a mixture of bromine vapour and oxygen cooled with liquid air in a tube.	The oxide is stable below $-40°C$ and less explosive than ClO_2. Decomposes into Br_2 and O_2 above 0°C.	The structure is similar to that of ClO_2.
Higher oxides of bromine (Bromine peroxide). [BrO_3 and Br_3O_8]	Both are formed as white crystalline solid by the action of pure ozone on pure Br_2-vapours at 0°C and low pressures.	These are not true peroxides, and they have not been fully characterised. They decompose with explosive violence.	Not exactly known.

Oxyacids of bromine : Two Oxy-acids of bromine are known. They are : (i) **hypobromous acid (HOBr)** and (ii) **bromic acid ($HBrO_3$).**

The best methods of the preparation of the oxyacids of bromine, together with some of their important properties are given in Table 18·7 :

TABLE 18·7

The oxyacids of bromine

Name and formula	Method of preparation	Important properties	Structure
Hypobromous acid ($HO\,Br$)	A aqueous soln. (6%) of hypobromous acid is prepared by shaking freshly precipitated HgO with Br-water, filtering the mixture and distilling the filtrate at 40°C under vacuum : $2HgO+2Br_2+H_2O=HgO.HgBr_2+2HOBr$. Pure $HOBr$ is obtained by distilling a mixture of Ag_2SO_4 and Br-water : $2Br_2+2H_2O+Ag_2SO_4=2AgBr+H_2SO_4+2HOBr$.	It is an unstable, weak acid and acts as an oxidising and a bleaching agent.	The structure of $HOBr$ is similar to that of hypochlorous acid.
Bromic acid ($HBrO_3$)	A soln. of bromic acid is prepared by the interaction of barium bromate and dil. H_2SO_4, or silver bromate and bromine water. The resultant precipitate of $BaSO_4$ or $AgBr$ is filtered off and the filtrate is concentrated in a vacuum desiccator : $Ba(BrO_3)_2+H_2SO_4=BaSO_4\downarrow+2HBrO_3$; $5AgBrO_3+3Br_2+3H_2O=5AgBr+6HBrO_3$.	Bromic acid is a powerful oxidising agent.	The structure of $HBrO_3$ is similar to that of $HClO_3$.

Some other properties of the oxyacids of bromine and their salts :

Hypobromous acid (HOBr) : The acid is much weaker than hypochlorous acid. Its aqueous solution is rapidly decomposed into bromic acid, bromine and oxygen, so that it is often coloured yellow :

$$5HOBr=HBrO_3+2Br_2+2H_2O\ ;$$
$$4HOBr=2Br_2+O_2+2H_2O.$$

The alkali metal salts of hypobromous acid or the alkali hypobromites are known in solution only. Their solutions are also very unstable and are converted into bromides and bromates on standing or warming : $3NaOBr=NaBrO_3+2NaBr$. As already stated, they are formed by the action of bromine on cold, dilute alkali solutions.

Bromic acid ($HBrO_3$) : As already stated, the solution of bromic acid acts as a strong oxidising agent and oxidises SO_2 and H_2S to sulphuric acid and liberates bromine from HBr :

$$2HBrO_3+5SO_2+4H_2O=Br_2+5H_2SO_4\ ;$$
$$8HBrO_3+5H_2S=4Br_2+4H_2O+5H_2SO_4\ ;$$
$$HBrO_3+5HBr=3Br_2+3H_2O.$$

Sodium and potassium bromates are obtained as sparingly soluble crystals on passing bromine vapour into hot, concentrated solutions of the corresponding alkalis :

$$3Br_2+6KOH=5KBr+KBrO_3+3H_2O.$$

Free Bromous acid ($HBrO_2$) is not known. But, alkali bromites are spontaneously formed by the decomposition of alkali hypobromite solutions : $2BrO^-=BrO_2^-+Br^-$. The resultant bromites are also very unstable and are readily transformed into bromates and bromides : $3BrO^-_2 \rightarrow 2BrO^-_3+Br^-$.

IODINE

Occurrence : Iodine is a comparatively rare element. The chief source of iodine is the crude Chile saltpetre or *caliche* which contains 0·2% of iodine as sodium iodate. The sea-weed and sponges contain small amounts of iodine which they obtain obviously from sea-water (containing approximately 0·001% iodine as iodides). Thyroxin hormone, an organic compound of iodine, is present in the thyroid gland of animals.

Isolation : Iodine is prepared in the laboratory by a method analogous to the preparation of chlorine and bromine, *i.e.* by distilling KI or NaI with MnO_2 and strong H_2SO_4 :

$$2KI+MnO_2+3H_2SO_4=2KHSO_4+MnSO_4+2H_2O+I_2.$$

The vapours of iodine are condensed in a cooled receiver. On a commercial scale, iodine is obtained either from *caliche* or from the burnt ashes (*kelp*) of sea-weeds.

(i) **Manufacture from caliche :** The mother-liquor of Chile saltpetre, after the removal of sodium nitrate, contains about 30% $NaIO_3$. On adding calculated amount of sodium bisulphite to this solution, iodine is precipitated. This is filtered, pressed and sublimed to get pure iodine :

$$2NaIO_3+5NaHSO_3=I_2\downarrow+3NaHSO_4+2Na_2SO_4+H_2O.$$

(ii) **Manufacture from kelp:** Burnt ashes of sea-weeds (kelp) contain about 1% iodine as iodide. The kelp is extracted with hot water and the filtered extract is concentrated. Any sulphates, chlorides or carbonates of sodium and/or potassium that crystallise out are removed and the mother-liquor is mixed with sulphuric acid.

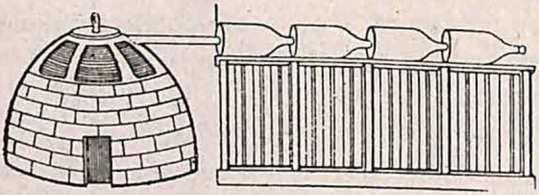


Fig. 18.10. Preparation of iodine from kelp.

Some sulphur may be deposited at this stage from the decomposition of sulphides. This is allowed to settle down and the decanted clear liquid is mixed with MnO_2 and distilled. Iodine distils over and it is collected in a series of crylindrical earthenware receivers called *aludels*.

The crude iodine, obtained as above, may be purified by sublimation, preferably after adding potassium iodide. Chemically pure iodine can be obtained by steam-distilling a solution of iodine in potassium iodide.

Properties: Iodine forms dark brown shining crystals (density = 4·94) with characteristic odour. It is volatile and sublimes on heating. [Above 700°C, the I_2 molecule dissociates: $I_2 \rightleftharpoons 2I$.] Although sparingly soluble in water, iodine readily dissolves in many organic solvents. [In carbon disulphide and carbon tetrachloride, iodine gives a violet solution; in benzene and chloroform, the colour of solution is purple; in alcohol and ether, the colour is brown. The difference in colour in different solvents is due to the association of the iodine molecules with the solvent. It also dissolves readily in aqueous KI, giving a deep brown solution containing the complex I_3^- ions.

Iodine resembles chlorine and bromine in chemical properties, but it is somewhat less reactive than the other two halogens. Solid iodine catches fire when brought in contact with white phosphorus, forming phosphorus tri-iodide : $2P+3I_2=2PI_3$. Metallic potassium combines with iodine with explosive violence. Iodine vapours also support the combustion of powdered arsenic, antimomy *etc.* When mercury is rubbed with iodine in a mortar, green Hg_2I_2 or yellow HgI_2 are formed, according to the amount of the two elements present. Hydrogen and iodine vapours combine partially at high temperatures to from hydrogen iodide : $H_2+I_2\rightleftharpoons 2HI$. It directly unites with the other halogens to form interhalogen compounds like IF_5, IF_7, ICl, ICl_3, IBr *etc.*

Iodine reacts with cold and dilute alkalis to form a mixture of iodide and hypoiodite : $2NaOH+I_2\rightleftharpoons NaI+NaOI+H_2O$. [The reaction is reversible.] With warm alkali solutions, iodine gives iodate and iodide : $3I_2+6NaOH=NaIO_3+5NaI+3H_2O$.

Iodine is a mild oxidising agent. It oxidises sulphurous acid, stannous chloride and sodium thiosulphate solutions :

$SO_2+I_2+2H_2O=H_2SO_4+2HI$; $SnCl_2+2HCl+I_2=SnCl_4+2HI$; $2Na_2S_2O_3+I_2=Na_2S_4O_6+2NaI$. [The last reaction is the basis of iodometric analysis.] When H_2S gas is passed through an aqueous suspension of iodine, sulphur is precipitated and hydroiodic acid is formed in solution : $I_2+H_2S=S\downarrow+2HI$. Unlike other halogens, iodine is oxidised by conc. HNO_3 to iodic acid : $3I_2+10HNO_3=6HIO_3+10NO+2H_2O$. With starch solution, iodine forms an intense blue colour which is an adsorption-complex of starch and iodine.

Uses : Iodine is used for the preparation of *tincture of iodine*. A solution of iodine is also used in volumetric analysis (*Iodimetry*). It is also used for the preparation of certain drugs, iodoform and some dyes.

Tests : Iodine gives violet vapours on heating and it dissolves in CS_2 or CCl_4 to give a violet soln. It forms a deep blue colour with starch soln. It also forms iodoform crystals on reaction with ethyl alcohol (or acetone) and caustic soda soln. Iodoform have characteristic smell.

COMPOUNDS OF IODINE

Hydrogen Iodide (HI).

Hydrogen iodide is prepared in the laboratory by dropwise addition of water on a mixture of red phosphorus and iodine. An apparatus similar to that used in the preparation of hydrogen bromide (see page 269 of this book) is generally employed. During the reactions, red phosphorus at first combines with iodine to produce PI_3, which is immediately hydrolysed by water to form phosphorous acid and hydrogen iodide : $2P+3I_2=2PI_3$; $PI_3+3H_2O=H_3PO_3+3HI$. The hydrogen iodide gas is freed from iodine vapours by passing it through a U-tube containing glass-beads smeared with moist red phosphorus, dried by passing through P_2O_5 or anhydrous CaI_2 and then collected by upward displacement of air. [As the gas attacks mercury, HI cannot be collected over it.]

Hydrogen iodide cannot be prepared by distilling an iodide with conc. H_2SO_4 due to its strong reducing action. HI reduces H_2SO_4 not only to SO_2 but also to sulphur and even to H_2S. The gas can, however, be prepared by heating solid alkali iodide with phosphoric acid :

$$3KI+H_3PO_4=K_3PO_4+3HI.$$

An aqueous solution of hydrogen iodide (hydroiodic acid) may be prepared by dissolving the gas in water through an inverted funnel (similar to the preparation of hydrochloric acid and hydrobromic acid). A convenient method for obtaining aqueous hydroiodic acid is, however, to pass H_2S gas through an aqueous suspension of iodine, and filtering off the precipitated sulphur : $I_2+H_2S=2HI+S\downarrow$.

Properties : A colourless gas with irritating smell, hydrogen iodide fumes in moist air and is very soluble in water, the aqueous solution being highly acidic. With water it forms a constant boiling mixture, having a boiling point of 127°C.

Hydrogen iodide has properties similar to HCl and HBr, but it is less stable. On exposure to sunlight, and on heating, it dissociates into the elements : $2HI\rightleftharpoons H_2+I_2$. It is easily oxidised so that a dry mixture of the gas with oxygen decomposes on exposure to sunlight to liberate iodine : $4HI+O_2\rightleftharpoons 2H_2O+2I_2$. Even a fresh aqueous solution (colourless) of the gas becomes brown in air due to oxidation into iodine. Hydroiodic acid, therefore, acts as a powerful reducing agent. If reduces sulphuric acid to sulphur dioxide, elemental sulphur and even to hydrogen sulphide ; nitric acid, iodic acid and hydrogen peroxide are also reduced ; ferric and cupric salts are reduced to the ferrous and cuprous salts respectively ; dichromate and permanganate are also reduced to the Cr^{+++} and Mn^{++} states ; chlorine and bromine are reduced to their hydracids ; alcohols are reduced to the corresponding hydro-

carbons : $H_2SO_4+2HI=I_2+2H_2O+SO_2$; $H_2SO_4+6HI=3I_2+4H_2O+S$; $H_2SO_4+8HI=4I_2+4H_2O+H_2S$; $2HNO_3+2HI=2H_2O+2NO+I_2$; $HIO_3+5HI=3H_2O+I_2$; $H_2O_2+2HI=2H_2O+I_2$; $2FeCl_3+2HI=2FeCl_2+2HCl + I_2$: $2CuSO_4+4HI=Cu_2I_2 + 2H_2SO_4+I_2$; $K_2Cr_2O_7+5H_2SO_4+6HI=Cr_2(SO_4)_3+2KHSO_4+7H_2O+3I_2$; $2KMnO_4+4H_2SO_4+10HI=2MnSO_4+2KHSO_4+8H_2O+5I_2$; $Cl_2+2HI=2HCl+I_2$; $Br_2+2HI=2HBr+I_2$; $C_2H_5OH+2HI \rightarrow C_2H_6+H_2O+I_2$.

Uses : Hydroiodic acid is used as a reducing agent in the laboratories.

Metal Iodides : These are metallic salts of hydroiodic acid. They are generally prepared by the action of the acid on the corresponding metal, or its oxide, hydroxide and carbonate. Some insoluble metal iodides are obtained by the addition of a solution of NaI, KI or HI to a solution of the metal salt concerned. Direct combination of the metal and iodine also produces some metal iodides All iodides, excepting those of Cu^+, Ag^+, Hg_2^{++}, Hg^{++} and Pb^{++}, are soluble in water.

Tests : (i) Hydroiodic acid or an iodide, on heating with conc. H_2SO_4, evolves violet vapours of iodine. (ii) Hydroiodic acid or a solution of an iodide liberates iodine on shaking with chlorine-water. The liberated iodine dissolves in CS_2 to form a violet soln. (iii) Hydroiodic acid or a solution of an iodide forms a yellow curdy ppt. with $AgNO_3$ soln. The ppt. is insoluble in HNO_3 and NH_4OH.

Iodide is estimated gravimetrically by weighing as AgI, or volumetrically by Volhard's method.

Oxides of Iodine.

Three oxides of iodine are known. These are :

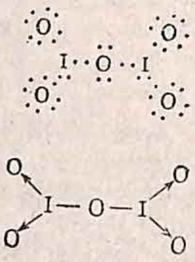
(i) **Iodine dioxide** (I_2O_4), (ii) **Iodine pentoxide** (I_2O_5) and (iii) **Iodine nona-oxide** (I_4O_9). Of these, the pentoxide is supposed to be the true oxide of iodine, while I_2O_4 is regarded as **iodyl iodate,** $(I^{III}O)^+ (I^{V}O_3)^-$ and I_4O_9 as **iodine tri-iodate,** $(I^{III})^{+3}$ $(I^{V}O_3{}^{3-}_{3}.)$

The method of preparation, important properties and the structure of the oxides are given in Table 18.8 :

Oxyacids of Iodine : Iodine forms three oxyacids, *viz.* (i) **hypoiodous acid (HIO),** (ii) **iodic acid (HIO_3)** and (iii) **periodic acid.** Three different types of periodic acid are known (along with their salts), and they are designated as (a) *para periodic acid* (H_5IO_6 or $HIO_4.2H_2O$), (b) *dimesoperiodic acid* ($H_4I_2O_9$) and (c) *meta-periodic acid* (HIO_4). None of the periodic acids are true peracids, as they do not contain the peroxo-grouping in their molecules. The different periodic acids may be looked upon as derived from the

TABLE 18.8

Oxides of Iodine

Name and formula	Method of preparation	Properties	Structure
Iodine dioxide (I_2O_4)	Prepared by heating iodic acid with conc. H_2SO_4 and decomposing the resultant basic sulphate with water.	A lemon-yellow powder, insoluble in water. Decomposes into I_2O_5 on heating : $5I_2O_4 = 4I_2O_5 + I_2$.	$\left[\mathrm{I^{III}O}\right]^{+}\left[\mathrm{I^{V}O_3}\right]^{-}$
Iodine pentoxide (I_2O_5)	Prepared by heating iodic acid at 200°C : $2HIO_3 = I_2O_5 + H_2O$.	It is a white powder, decomposing at 500°C: $2I_2O_5 = 2I_2 + 5O_2$. It is the anhydride of iodic acid, as it dissolves in water to produce the acid. It is a strong oxidising agent and oxidises carbon monoxide to carbon dioxide : $5CO + I_2O_5 = I_2 + 5CO_2$.	
Iodine nona-oxide (I_4O_9)	Prepared by the action of ozonised oxygen on iodine at 40°C.	A pale yellow, deliquescent powder. Decomposes by water into iodic acid and iodine. On heating, I_2O_5 is formed.	$\left[\mathrm{I^{III}}\right]^{+3}\left[\mathrm{I^{V}O_3}\right]_3^{3-}$

hypothetical acid anhydride, I_2O_7, by the successive addition of H_2O molecule.

(i) **Hypoiodous acid (HIO)** : It is a very unstable acid, and a dilute aqueous solution (pale greenish yellow) of it is transiently obtained by shaking precipitated HgO and iodine with water and filtering the mixture : $2I_2 + 2HgO + H_2O = HgO.HgI_2 + 2HIO$. It is a very weak acid and it readily disproportionates to iodic acid and iodine : $5HIO = HIO_3 + 2I_2 + 2H_2O$. Its structure is similar to HOCl.

The alkali metal salts of hypoiodous acid (the alkali hypoiodites) are obtained by dissolving iodine in cold dilute alkali solutions : $I_2 + 2KOH = KI + KIO + H_2O$. These salts are known only in solution, and have not been isolated in the pure state. They are not also very stable in solution, but are easily hydrolysed :

$KIO+H_2O \rightleftharpoons KOH+HIO$. Their solutions have characteristic smell and give a blue colour with KI-starch paper in absence of alkali. They are less stable than the corresponding hypochlorites and hypobromites and as such, are more powerful oxidising agents than the latter.

(ii) **Iodic acid (HIO_3) :** This is the most stable oxyacid of iodine and is more stable than chloric and bromic acids. The acid is best prepared by boiling iodine with excess (about 10 times the weight of I_2 taken) of concentrated HNO_3 of sp. gr. 1·5. The resultant liquid is evaporated to dryness at 200°C to remove HNO_3. Iodic acid is simultaneously dehydrated to iodine pentoxide, which is then dissolved in minimum quantity of warm water. On cooling the solution, white crystals of iodic acid separate :

$$3I_2+10HNO_3=6HIO_3+10NO+2H_2O.$$

Iodic acid can also be obtained by heating salts of iodic acid (such as sodium iodate, barium iodate *etc.*) with dilute sulphuric acid, or by evaporating chloric acid with iodine, or by oxidising iodine by means of chlorine in aqueous solution. [Hydrochloric acid produced simultaneously in the last reaction is removed by adding silver oxide.]

$NaIO_3+H_2SO_4=NaHSO_4+HIO_3$; $2HClO_3+I_2=2HIO_3+Cl_2$; $I_2+5Cl_2+6H_2O=2HIO_3+10HCl$.

Properties : The colourless, lustrous crystals of iodic acid have bitter taste. When heated, the crystals partially melt at 110°C to form a product poorer in water (or the lower hydrate, as it may be called), commonly known as *anhydroiodic acid* [HI_3O_8 or $(I_2O_5)_3, H_2O$] ; On heating to 195°C, all the water is lost and iodine pentoxide remains as a white powder :

$$6HIO_3=(I_2O_5)_3.H_2O+2H_2O\uparrow \ ; \ (I_2O_5)_3.H_2O=3I_2O_5+H_2O\uparrow.$$

Iodic acid is a strong oxidising agent. Powdered charcoal, phosphorus, sulphur or organic matter catch fire when heated with the solid acid. Aqueous solution of the acid oxidises sulphur dioxide, hydrogen sulphide and hydroiodic acid :

$$2HIO_3+5SO_2+4H_2O=5H_2SO_4+I_2\downarrow \ ;$$
$$2HIO_3+5H_2S=5S\downarrow+6H_2O+I_2\downarrow \ ;$$
$$HIO_3+5HI=3H_2O+3I_2.$$

The aqueous solution of the acid dissolves metals like Zn, Mg, Fe, Al *etc.* to form the corresponding metal iodates, liberating hydrogen (which partially reduces the iodates to iodides). Litmus paper is first turned red and then bleached by a solution of HIO_3. Although HIO_3 is a monobasic acid, it forms *bi-salts* as $KIO_3 . HIO_3$; $KIO_3 . 2HIO_3$ *etc.* The structure of iodic is similar to that of of chloric acid.

Iodates of alkali metals (such as $NaIO_3$ and KIO_3) are formed, along with the corresponding iodides, by the reaction of iodine with hot, concentrated alkali solutions. Potassium iodate, however, is generally prepared by heating iodine with a concentrated solution of potassium chlorate in presence of a small amount of nitric acid :

$$2KClO_3+I_2=2KIO_3+Cl_2\uparrow .$$

[This is due to the fact that the more electropositive iodine has a greater affinity than chlorine for oxygen.]

Iodates are good oxidising agents. They decompose on heating into iodide and oxygen (or into iodine, oxygen and the oxide of the metal). Barium iodate, however, forms barium periodate, iodine and oxygen on heating :

$$KIO_3=2KI+3O_2\uparrow ; \qquad 2Ca(IO_3)_2=2CaO+2I_2\uparrow+5O_2\uparrow ;$$

$$5Ba(IO_3)_2=Ba_5(IO_6)_2+4I_2\uparrow+9O_2\uparrow .$$

A mixture of iodate and iodide liberates iodine quantitaively on acidification :

$$IO_3^-+5I^-+6H^+=3I_2+3H_2O.$$

So, such a mixture can be used for the estimation of an acid by titrating the liberated iodine. The acid salt, potassium bi-iodate ($KIO_3 . HIO_3$) is sometimes employed as a standard for acidimetry and alkalimetry.

Periodic acids : The best-known of the periodic acids is paraperiodic acid, H_5OI_6, which may be looked upon as the 5-hydrate, $I_2O_7.5H_2O$. It is prepared by reacting the silver salt of the mesoperiodic acid, Ag_3IO_5, with chlorine, and crystallising the filtrate : $4Ag_3IO_5+6Cl_2+10H_2O=4H_5IO_6+12AgCl+3O_2$. A better method involves the reaction between barium paraperiodate and concentrated HNO_3 and crystallisation after removal of precipitated barium nitrate.

The acid is prepared on a large scale by the electrolysis of iodic acid at a low temperature in a porous cell (placed in a vessel of dil. H_2SO_4) with lead peroxide anode and platinum cathode. Deliquescent crystals of the acid are obtained from the anodic solution after the electrolysis.

Paraperiodic acid forms colourless monoclinic crystals, melting at 140°C with decomposition into iodic acid, water and oxygen (plus some ozone) : $2H_5IO_6=2HIO_3+4H_2O+O_2$. At 80°C under vacuum, this acid loses water to form the 2-hydrate or the dimesoperiodic acid ($I_2O_7.2H_2O$ or $H_4I_2O_9$) and at 100°C, the 1-hydrate or the metaperiodic acid ($I_2O_7.H_2O$ or HIO_4) results :

$$2H_5IO_6 \rightarrow 3H_2O + H_4I_2O_9$$
$$\downarrow$$
$$2HIO_4 + H_2O.$$

Metaperiodic acid sublimes on further heating at 110°C.

Paraperiodic acid is highly soluble in water and acts as a strong monobasic acid. [It also behaves sometimes as a weak dibasic acid.] The aqueous solution slowly decomposes with the liberation of ozonised oxygen.

All the periodic acids are strong oxidising agents (more powerful than iodic acid). In nitric acid solution, they oxidise manganous salts to permanganates and liberate iodine from neutral or acidic solutions of potassium iodide.

Periodates or the salts of periodic acids can be obtained by direct or indirect methods. Like the parent acids, the salts are also strong oxidising agents and are often used as such. Periodates derived from all the periodic acids are known; in addition, salts of unknown periodic acids like H_3IO_5 (mesoperiodic acid) have also been isolated. But, the commonest of all these salts are the paraperiodates and the metaperiodates.

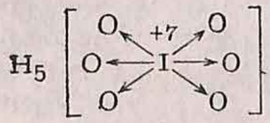
Disodium paraperiodate ($Na_2H_3IO_6$) is prepared by passing chlorine gas into a boiling solution of iodine in NaOH solution. Sodium iodate, which is formed at the first stage, is subsequently oxidised to the periodate. Sparingly soluble crystals of the salt separate out from the hot liquid :

$$NaIO_3 + 3NaOH + Cl_2 = Na_2H_3IO_6 + 2NaCl.$$

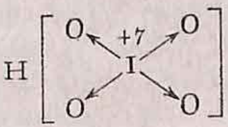
When $AgNO_3$ solution is added to an aqueous suspension of $Na_2H_3IO_6$ at 100°C, black insoluble **silver mesoperiodate** (Ag_3IO_5) is formed : $Na_2H_3IO_6 + 3AgNO_3 = Ag_3IO_5\downarrow + 2NaNO_3 + HNO_3 + H_2O$.

Potassium metaperiodate (KIO_4) is generally obtained as colourless, sparingly soluble crystals by the anodic oxidation of potassium iodate in caustic potash solution.

The following structures have been proposed for paraperiodic acid and metaperiodic acid.



H_5IO_6



HIO_4

Electropositive iodine and its compounds: We have already pointed out that, coming towards the lower end of the halogen series, iodine possesses considerable electropositive character. As a result, this halogen forms many compounds (simple or complex), in which it is supposed to exist as I^+ or I^{+3}.

(1) **Evidence for I^+:** Molten ICl conducts electricity, and on electrolysis, only iodine is liberated at the cathode, while both iodine and chlorine are set free at the anode. It is presumed that ICl ionises as, $2ICl \rightleftharpoons I^+ + ICl_2^-$ in this case. Molten ICN behaves similarly during electrolysis. Further, as an electrophilic iodinating agent, ICl attacks acetanilide at sites having excess electron, to produce 4-iodoacetanilide. Hence, iodine in ICl must be the positive counterpart.

Hypoiodous acid is amphoteric, behaving both as an extremely weak acid and an extremely weak base. The dissociation of the compound in these cases is supposed to be: $HIO \rightleftharpoons H^+ + IO^-$ and $HIO \rightleftharpoons I^+ + OH^-$. In the latter case, iodine in HIO behaves as a univalent positive element.

When a solution of iodine in an inert solvent is passed through a column of cationic ion-exchange resin, some iodine is retained on the resin: H^+ Resin$+I_2 \rightarrow I^+$ Resin$+$HI. This provides another proof of the existence of I^+.

A number of comparatively stable compounds of monopositive iodine can be obtained through co-ordination with neutral molecules like pyridine. Complexes of the composition $I(py)NO_3$, $I(py)_2NO_3$, $I(py)ClO_4$, I(py) acetate and I(py) benzoate are known. [A solution of $I(py)_2NO_3$ in chloroform liberates iodine at the cathode on electrolysis.]

(2) **Evidence of I^{+3}:**

Electrolysis of ICl_3 in the molten state liberates Cl_2 and I_2 at both the electrodes. This indicates ionization of the compound as, $2ICl_3 \rightleftharpoons ICl_2^+ + ICl_4^-$. Compounds of tripositive iodine like iodyl sulphate, $(IO)_2SO_4$, iodine nitrate, $I(NO_3)_3$, iodine phosphate, IPO_4 and iodine acetate, $I(CH_3COO)_3$ have also been prepared. When iodine acetate is electrolysed with Ag-electrodes, one equivalent of AgI is formed at the cathode for every 3 Faradays of electricity passed. This observation shows that the compound ionises as, $I(CH_3COO)_3 \rightleftharpoons I^{+3} + 3(CH_3COO)^-$.

Interhalogen compounds.

Due to their comparable electronegativities, the different halogen elements combine with one another to form interhalogen compounds which are mostly covalent in nature because of the small electronegativity difference between the component elements. Their melting and boiling points increase as the difference in electronegativity increases, indicating the increase in ionic character.

All the interhalogen compounds are prepared by direct combination of the elements, or by the action of a halogen on a lower interhalogen. The formation of the products depends upon the condition of the reactions. Not more than two different halogens occur in a molecule of an interhalogen. These compounds can be classified into four types, *viz*. (i) Diatomic (AB), (ii) Tetratomic (AB_3) (iii) Hexatomic (AB_5) and (iv) Octatomic (AB_7). In all the cases, the element A is the less electronegative element with larger atomic volume.

Interhalogen compounds of the types AB and AB_3 are formed by the halogens whose electronegativity difference is not too great. AB_5 and AB_7 types of the compounds are formed by the larger atoms like Br and I with the smaller atoms like F. Some physical properties of these compounds are given in Table 18.9 :

TABLE 18.9

Interhalogen Compounds

AB type	AB_3 type	AB_5 type	AB_7 type
ClF : Colourless gas. **BrF** : Reddish brown unstable gas. **BrCl** : Extremely unstable. **ICl** : Stable red crystals, m.p. 27·2°C. **IBr** : Black crystals.	**ClF_3** : Colourless fuming liquid, b.p. 13°C. **BrF_3** : Colourless fuming liquid, b.p. 127°C. **ICl_3** : Lemon yellow crystals ; dissociates on heating : $ICl_3 \rightleftharpoons ICl + Cl_2$.	**BrF_5** : Colourless liquid, b.p. 41°C. **IF_5** : Colourless solid, m.p. 9°C, b.p. 97°C.	**IF_7** : Colourless gas, solidifies at 4°C.

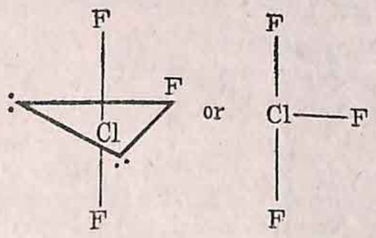
The interhalogen compounds are more reactive than the halogens (except F, of course) due to the fact that A – B bond is weaker that A–A or B–B bonds in the halogens. The reactions of the interhalogen compounds are similar to those of the halogens. They are hydrolysed by water to form halide and oxyhalide ions, the latter being formed from the larger halogen atom present in the molecule :

$$BrF_5 \xrightarrow{H_2O} 5F^- + BrO_3^- + H^+.$$

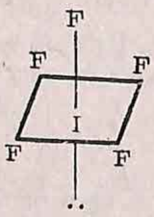
Iodine monochloride is the best-known compound of the AB type. It is formed by the action of Cl_2 on iodine. With excess Cl_2, iodine trichloride is formed. Both ICl and ICl_3 are hydrolysed by water : $5ICl+3H_2O=2I_2+HIO_3+5HCl$; $2ICl_3+3H_2O=ICl+HIO_3+5HCl$. This ICl can undergo futher hydrolysis as shown before. With alkalis, they give iodides and iodates : $3ICl+6KOH=3KCl+2KI+KIO_3+3H_2O$; $3ICl_3+12KOH=9KCl+KI+2KIO_3+6H_2O$. These reactions occur due to the disproportionation of I^+ into I^0 and I^{+5} and that of I^{+3} into I^- and I^{+5}.

Iodine monochloride is used for the estimation of 'iodine number' of fats and oils. It is also used to iodinate organic compounds.

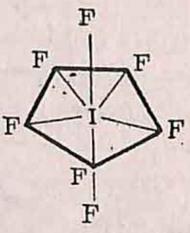
The structures of AB type interhalogens are linear ; those of AB_3 type are trigonal bipyramid (sp^3d hybridisation) with two apices of the triangular base occupied by two lone-pairs of electrons (*i.e.* T-shaped) ; the AB_5 type compounds are either octahedral (sp^3d^2 hybridisation) with one apex of the octahedron occupied by a lone-pair of electrons (or it may be square-pyramidal) ; the AB_7 type of the compounds have pentagonal bipyramidal structure.



AB_3-type compounds



AB_5 - type



AB_7- type

Polyhalides : It is a known fact that solutions of potassium iodide or sodium iodide readily dissolves iodine to give a deep brown solution. In a similar manner, solutions of alkali bromides are capable of dissolving a considerable amount of bromine and even iodine. It has been shown that the above solutions contains complex anions, consisting of three or more halogen atoms, *viz*. I_3^-, Br_3^-, BrI_2^- etc., and their formation may be represented as :

$$I^- + I_2 = I_3^- \;;\; Br^- + Br_2 = Br_3^- \;;\; Br^- + I_2 = BrI_2^-.$$

Similar polyhalide ions, containing three different halogens (*e.g.*, $IBrF^-$, $IBrCl^-$) may be formed by the reaction between a metal halide and an interhalogen. The Br_3^- ion is much less stable than I_3^- ion, and compounds containing Cl_3^- ions are even more unstable. No compounds containing F_3^- ions are known. [This is probably due to the non-availability of *d*-orbitals for fluorine, which precludes its expansion of octet.]

Many solid crystalline polyhalides and mixed polyhalides are known. They are typically ionic compounds, and can be prepared by the direct union of halogens (or interhalogens) with metal halides : $KI + Cl_2 = KICl_2$; $KICl_2 + Cl_2 = KICl_4$. Polyhalides, generally tend to decompose on heating :

$$CsI_3 \xrightarrow{\text{heat}} CsI + I_2 \;;\; RbICl_2 \xrightarrow{\text{heat}} RbCl + ICl.$$

But, the polyhalides of the type $MICl_4$ are the most stable compounds (even the free acid $HICl_4$ is known).

Structures of the tri-halide ions of the type I_3^-, ICl_2^-, $IBrF^-$ are linear. The structures of pentahalide ions like ICl_4^-, BrF_4^- are square-planar.

Pseudo halogens or Halogenoids.

A pseudohalogen or halogenoid is a molecule consisting of more than two electronegative elements which, in the free state, possesses properties comparable to those of the elemental halogens, and in the form of anions possesses properties comparable to those of the halide ions. The pseudohalogen anions combine with hydrogen to form an acid and with silver to form a salt insoluble in water. The well-known pseudo-halogens are cyanogen, $(CN)_2$; thiocyanogen, $(SCN)_2$, selenocyanogen, $(SeCN)_2$ *etc.* Some of them have been discussed in Chapter XV of this book. The following are the similarities between pseudo-halogens and halogens : (i) Pseudo-halogens are volatile substances consisting of symmetrical combination of two pseudo-halide radicals, X–X ; (ii) They combine with various metals to form salts containing X^- anions : (iii) The silver, mercurous and lead salts of them are insoluble in water ; (iv) The hydracid HX is known ; (v) They form covalent compounds analogous to covalent halides ; (vi) X^- ions are oxidised to X_2 by suitable oxidants ; (vii) The pseudo-halide ions form metallic complexes like the halide ions and (viii) Their ions form complexes with themselves and also with the halogens.

CHAPTER XIX

THE TRANSITION ELEMENTS

What are the transition elements ?

The *transition elements* are characterized by atoms (or ions) in which the *d-level of the penultimate shell* is occupied, but not filled to capacity. They are also known as the *'d'-block elements*, as the atoms of these elements receive their *last electrons*, (also known as the *differentiating electrons* ; see vol. I, p. 112) in the *d*-level.

Why are they so called ?

In the long form of the periodic table (Table 2.3, Vol. I, p. 110), these '*d*'-block elements are placed in between the '*s*'-block and the '*p*'-block elements. Because of their position in between the '*s*'-and '*p*'-block elements, they exhibit properties *intermediate* between those of the highly reactive and electropositive '*s*'-block elements of Gr. IA and Gr. IIA, exhibiting strongly ionic character, and the '*p*'-block elements which mostly form covalent compounds.

Electronic configurations : The general electronic configuration of the atoms of the transition elements in their valence-shell may be written as $ns^2(n-1)d^{1-9}$, where the presence of two electrons in the *ns*-level is not always adhered to. Thus, chromium has a valence-shell configuration of $3d^5 4s^1$ and palladium has $4d^{10} 5s^\circ$.

The reasons for the gradual filling up of an inner d-level prior to the filling up of the outermost p-level, can be clearly understood from the discussion on the energy order of the orbitals and Hund's rule of maximum multiplicity (see Vol. I, pp. 96-100).

As pointed out previously (Vol. I, p. 111), *four* transition series occur among the elements of the periodic table, corresponding to the gradual filling up of the 3*d*, 4*d*, 5*d* and 6*d* levels. Corresponding to the complete filling up of these '*d*'-levels by ten electrons, each transition series comprises of ten elements. The fourth transition series contains the radioactive and rather unfamiliar elements, whose valence-shell electronic configurations are somewhat complicated. They are excluded from the present discussion. The following table contains the first three transition series. The atomic numbers and the valence-shell electronic configuration of the members of the first transition series are also included.

TABLE 19.1

	III A	IV A	V A	VI A	VII A ←		VIII		→ IB	IIB
1st transition series. The 3d-level is being filled up.	21 Scandium Sc $3d^14s^2$	22 Titanium Ti $3d^24s^2$	23 Vanadium V $3d^34s^2$	24 Chromium Cr $3d^54s^1$ *	25 Manganese Mn $3d^54s^2$	26 Iron Fe $3d^64s^2$	27 Cobalt Co $3d^74s^2$	28 Nickel Ni $3d^84s^2$	29 Copper Cu $3d^{10}4s^1$ *	30 Zinc Zn $3d^{10}4s^2$
2nd transition series. The 4d- level is being filled up.	39 Yttrium Y	40 Zirconium Zr	41 Niobium Nb	42 Molybdenum Mo	43 Technitium Tc	44 Ruthenium Ru	45 Rhodium Rh	46 Palladium Pd	47 Silver Ag	48 Cadmium Cd
3rd transition series. The 5d- level is being filled up.	57 Lanthanum La †	72 Hafnium Hf	73 Tantalum Ta	74 Tungsten W	75 Rhenium Re	76 Osmium Os	77 Iridium Ir	78 Platinum Pt	79 Gold Au	80 Mercury Hg

* For explanation of these rather unusual configurations, see Vol. I., pp. 99-100.

† The fourteen rare earth elements occur between La and Hf. See Vol. I, pp. 111-113.

Why are the Gr. IB and the Gr. IIB elements often included in the family of the transition elements ?

It can be seen from the above table that, each transition series begins with a Gr. III A element and, *conceptually*, ends with the last member of the Gr. VIII triads. Thus, according to the concept of the presence of *incompletely* filled *d*-orbitals, the Gr. IB elements (Cu, Ag and Au), the Gr. II B elements (Zn, Cd and Hg) and even palladium (with $4d^{10}$ $5s^{\circ}$ configuration) should not be considered as *true transition elements*. However, in a few of their common oxidation states, some of these metals possess incompletely filled *d*-orbitals (e.g. Cu^{+2} has a d^9-and Pd^{+2} has a d^8-configuration) and hence, they exhibit many characteristic properties of the true transition metals. The Gr. II B elements (Zn, Cd and Hg) possess d^{10}-configuration in their stable (and often only) oxidation state of +2 and hence, exhibit some perceptible differences from the other members. However, they do possess some characteristics of the transition metal ions like the capacity of complex formation, catalytic activity etc., and are considered as the end-members of the transition series. It may be observed here that, some characteristics of the transition elements are *carried over* to the members of the Gr. II B elements.

The transition metals vary widely in their extent of occurrence in the earth's crust. Iron, titanium, vanadium and chromium are present in quite large quantities, while metals like scandium and rhenium are rather rare. Many transition elements, even though they are rather abundant, are unfamiliar to us because of the difficulty involved in the extraction of those elements from their available ores. Zirconium, which is as abundant as chromium, is such an element. It should be noted that the technical economy of the entire world rests mostly on certain transition metals like titanium, chromium, iron, nickel, copper zirconium, molybdenum and tungsten.

General properties of the transition elements.

The transition elements form a well-knit series, having several common properties. In the atoms of the transition elements, the last electrons are gradually added to *the d-level of the penultimate shell*, keeping *the configuration in the outermost shell* constant (more or less). Hence, it is quite expected that those physical and chemical properties of the transition elements, which primarily depend on the outermost electronic configuration, will be similar. The magnitude of variation of those properties among the individual members of a transition series (especially among the adjacent members) should be much less marked than what is found among the representative elements of a particular period. The common properties possessed by all the transition elements are mentioned below :

1. All the transition elements are metals, hard, strong, high melting and high boiling.

2. They form alloys with many other metals and among themselves.

3. They are good conductors of heat and electricity.

4. Most of them are sufficiently electropositive or "active" to dissolve in mineral acids. But, a few have low electrode-potentials and are not affected by ordinary acids. Such *noble* metals are Cu, Ag, Au (Gr.IB) and Pd and Pt (Gr. VIII). They are attacked only by the strongly oxidising acids (e.g. HNO_3, aqua regia).

5. Most of them exhibit variable valence and their ions are coloured in majority of the oxidation states in which they occur.

6. Because of the presence of unpaired electrons in the incomplete *d*-orbitals, they form at least one or two **paramagnetic compounds*.

Most of the special characteristics of the transition elements are due to the presence of d-electrons.

In transition elements, *the d-orbitals project out to the periphery of the atoms or ions*. As a result, the electrons residing in these *d*-orbitals are strongly perturbed or affected by the immediate environment in which the atoms or ions are present. In their turn, these *d*-electrons also exert their influence on their surroundings. Hence, a number of characteristic properties of the transition metal atoms or ions are very much dependent *on the exact number* and the *actual arrangement* of the electrons. Most of the special properties of the transition elements, therefore, can be attributed to the presence of *d*-electrons in the penultimate shell.

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* See under the heading 'magnetic properties' on pages 294-295.

We shall now proceed to discuss the more important properties of the transition elements under specific headings. In this discussion, we will confine ourselves to the discussion on the *first transition series* and mention about some members of the second and third transition series only, when it is really necessary and truly relevant.

As pointed out before, the members of the first transition series are similar to each other in several ways. The following table contains some of their important characteristics :

TABLE 19.2

Properties	III A	IV A	V A	VI A	VII A	←VIII→			I B	II B
	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Zn	30 Zn
Electronic configuration (in the two outermost levels).	$3d^1 4s^2$	$3d^2 4s^2$	$3d^3 4s^2$	$3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^{10} 4s^1$	$3d^{10} 4s^2$
Atomic radius (Å)	1.44	1.32	1.22	1.17	1.17	1.16	1.16	1.15	1.17	1.25
Ionization energy (Kcals)										
1st	151	158	155	156	171	182	181	176	178	217
2nd	297	314	328	380	361	373	393	419	468	414
3rd	571	649	685	714	777	707	772	811	849	915
Ionic radii (Å) and electronic configuration : M^{+2}	—	($3d^2$) 0.90	($3d^3$) 0.88	($3d^4$) 0.84	($3d^5$) 0.80	($3d^6$) 0.76	($3d^7$) 0.74	($3d^8$) 0.72	($3d^9$) 0.72	($3d^{10}$) 0.74
M^{+3}	$3d^0$ 0.81	($3d^1$) 0.76	($3d^2$) 0.74	($3d^3$) 0.69	($3d^4$) 0.66	($3d^5$) 0.64	($3d^6$) 0.63	—	—	—
Reduction potential (volts)										
$M^{+2}+2e \rightleftharpoons M$	—	−1.6	−1.2	−0.91	−1.18	−0.44	−0.28	−0.25	+0.34	−0.76
$M^{+3}+3e \rightleftharpoons M$	−2.1	−1.20	−0.85	−0.74	−0.28	−0.04	0.04	—	—	—
M.P. (°C)	1522	1677	1917	1903	1244	1539	1495	1455	1083	420
B.P. (°C)		3277	3377	2627	2067	2877	2877	2887	2582	907

Atomic and ionic radii : From the data given in Table 19.2, it is clear that the atomic radii of the members of the first transition series gradually decrease with the increase in atomic number. The reason is obvious. The electrons are gradually added to an inner level (3*d*, without creating new outer levels) and the increased nuclear positive charge pulls the electrons inward, resulting in a contraction of volume. A similar trend is also observed in the case of the M^{+2} and M^{+3} ions of the transition elements due to the same reason.

Ionization energies and electronegativities : A slow but gradual decrease in atomic volume and increase in nuclear charge should lead to a parallel increase in the ionization energies. The general trend in the case of 1st, 2nd and 3rd ionization energies follows this pattern with some exceptions thrown in-between. In most cases, the values are between those of *s*-and *p*-block elements. This is an indication of the fact that, the transition elements are generally less electropositive than the Gr. IA and IIA elements, but are more basic than the elements of the Groups III B onwards. It also indicates that transition metals have a fair tendency to form ionic compounds which are less ionic than those of Gr. I A or II A metals. In addition, due to their rather small ionic radius and comparatively large ionic charge (especially in their higher oxidation states), they will be able to form covalent compounds as predicted by Fajan's rules of ionic distortion. This tendency is reflected in the following electronegativity data :

TABLE 19.3

Element	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Electronegativity in the most stable oxidn. state	1.5	1.6	1.6	1.5	1.8	1.8	1.8	1.9	1.6

Reactivity : Since the transition metals have low atomic volumes and fairly high ionization energies and have the tendency to form covalent bonding, they have high values of the heat of sublimation. Thus, considerably large amount of energy is necessary to take them to the vapour state. High sublimation energies and large ionization energies re-inforce each other to make the transition metals rather unreactive in comparison to the metals of the representative elements. This tendency is well-marked in copper and attains its highest peak in palladium, gold and platinum.

The rather low reactivity of most of these metals with hydrogen ion (H^+) is indicated in the magnitude of the reduction potentials given in Table 19·2. The +ve sign of the reduction potential in the case of copper indicates that it does not react with H^+.

Melting and boiling points : The melting and boiling points of the transition metals are much higher than the representative elements. Most of them have melting points above 1000°C. The presence of incompletely filled *d*-orbitals and the resultant tendency to form strong covalent bonding among the atoms of a transition metal are responsible for their high melting and boiling points.

Oxidation states : The transition metals exhibit quite a large number of oxidation states, which are closely linked to their electronic configurations. The different oxidation states of the members of the first transition series, along with their electronic configurations, are given in the table 19·4. The most stable oxidation states are given in bold types.

As the difference in energy between the $(n-1)d$ and *ns*-orbitals is small (and within the range of the energy involved in chemical bond formation), electrons from one or both of these orbitals can be utilised for bonding. This is the reason for the existence of variable oxidation states in transition metals in contrast to the rather fixed oxidation states observed in the case of the representative elements.

Certain generalisations can be made from the data given in table 19·4. These are :

(i) The minimum oxidation state of a transition element is generally equal to the number of *ns*-electrons in that atom. Thus, +2 is the minimum oxidation state for Ti, V, Mn, Fe, Co, Ni and Zn, all of which have 2 electrons in the *ns*-level. The other transition elements have ns^1 configuration and hence, Cr, Cu (as also Au, Ag) possess minimum oxidation state of +1.

(ii) The maximum oxidation state for each of the transition elements of Grs. IIIA to VIIA, is equal to the group number and is numerically equal to the total number of $(n-1)d$ and ns-electrons in that atom. However, most of the elements in Gr. VIII shows a maximum oxidation state of +6, with ruthenium and osmium exhibiting a maximum oxidation state of +8.

TABLE 19·4

Transition elements and their atomic numbers	Oxidation states with electronic configurations										
	$3d^{0}$	$3d^{1}$	$3d^{2}$	$3d^{3}$	$3d^{4}$	$3d^{5}$	$3d^{6}$	$3d^{7}$	$3d^{8}$	$3d^{9}$	$3d^{10}$
Scandium Sc–21	3+										
Titanium Ti–22	4+	3+	2+								
Vanadium V–23	5+	4+	(3+)	2+							
Chromium Cr–24	6+	5+	4+	3+	2+	1+					
Manganese Mn–25	7+	6+		4+	3+	2+					
Iron Fe–26			6+		4+	3+	2+				
Cobalt Co–27							3+	2+			
Nickel Ni–28							4+	3+	2+		
Copper Cu–29									3+	2+	1+
Zinc Zn–30											2+

(iii) The number of oxidation states displayed by a transition metal gradually increases from left to right in each transition series, becomes maximum at the middle (i.e. at d^5s^2-configuration) and then again decreases towards the end of the series. Thus, in the first transition series, manganese has the largest number of oxidation states (from+7 to+2), while zinc has only one oxidation state of+2. This is why *manganese is sometimes referred to as the* **most versatile element** *in the periodic table.*

Stability of the different oxidation states : The relative stabilities of the different oxdiation states of the first row transition metals (and also those of the 2nd and 3rd transition series) may partially be attributed to the extra stability of the $3d^\circ$ (unfilled d-level), $3d^5$ (half-filled) and $3d^{10}$ (full-filled d-level) configurations. Thus, Ti^{+4} (d°) is more stable than Ti^{+3} (d^1), and Mn^{+2} (d^5) is much more stable than Mn^{+3} (d^4). However, such generalisation can not be made in the cases of all the members of this series and it is very little applicable in the case of the 2nd and 3rd transition series of elements.

The higher oxidation states of the first transition series are strong oxidising agents and more so, if they exist as oxy-anions. Thus, MnO_4^-, CrO_4^{2-} and $Cr_2O_7^{2-}$ are all very strong oxidising agents. Co^{+3} and Ni^{+4} (and to some extent Ni^{+3}) are also strong oxidising agents. The lower oxidation states of +2 and +3 are of real importance in the case of the first row transition elements. It may be noted here that in a particular sub-group, the stability of of the higher oxidation states increases and that of the lower oxidation states decreases with the increase in atomic number.

It may also be pointed out here that, the covalent character of a particular compound of a transition metal increases with the increase in the positive oxidation state, following Fajan's rules of ionic distortion. Thus, $FeCl_3$ is more covalent than $FeCl_2$. Similarly, the acidity is also increased with the increase in positive oxidation state, *e.g.* Fe^{+3} compounds are more acidic than Fe^{+2} compounds.

Magnetic properties : A substance which is attracted into a magnetic field is called **paramagnetic**, and this paramagnetism is due to the presence of one or more *unpaired electrons* in the atom, molecule or ion of that substance.

A diamagnetic substance is repelled by a magnetic field and is a characteristic of the presence of completely filled up electronic levels. All forms of matter exhibits diamagnetism to some extent at least.

The magnetic moment is expressed in units of Bohr Magnetons (B. M.), which is defined by, B. M.$=\frac{eh}{4\pi\, mc.}$, where h is the Planck's constant, e is the electronic charge, m is the electronic mass and c is the velocity of light. The effective magnetic moment ($\mu_{eff.}$) of a substance containing 'n' unpaired electrons (and no other contribution towards its magnetic property) is given by $\mu_{eff}=\sqrt{n(n+2)}$ B.M. Hence, the effective magnetic moment varies with the number of unpaired electrons in it. The magnetic moments due to 1, 2, 3, 4 and 5 electrons (calculated with the help of the above relation) are 1.73, 2.84, 3.57, 4.90 and 5.92 B.M. respectively.

From the data included in Table 19·4, it is clear that in majority of the oxidation states, the ions of the transition metals are paramagnetic in nature due to the presence of variable numbers of unpaired electrons. Thus, all ions with d^1 and d^9 configurations (e.g. Ti^{+3}, V^{+4}, Cr^{+5}, Mn^{+6}, Cu^{+2}) will have $\mu_{eff}\sim 1.73$ B.M.

Colour : Majority of the known transition metal compounds are coloured in the solid state or in solution. It has been established that these colours are due to the presence of incompletely filled d-orbitals in the ions of the transition metals. The transition metal ions, having *completely vacant* d-orbitals (as in Sc^{+3}) and *completely filled* d-orbitals (as in Cu^{+1}, Ag^{+1}), are colourless. Most of the compounds of the representative elements of the *s*- and *p*-blocks are colourless due to the same reason.

Catalytic properties : Majority of the transition metals and many of their compounds exhibit remarkable catalytic properties. Platinum, iron, iron oxides, vanadium pentoxide, nickel, molybdenum metal and oxides, oxides of chromium etc. are some familiar examples. Platinum metal and V_2O_5 are good catalysts for the manufacture of SO_3 from SO_2. Iron, coupled with Mo and Cr, acts as a catalyst in the combination of nitrogen and hydrogen to ammonia by the Haber's process, and nickel (also platinum) is used as the catalyst in the hydrogenation processes.

The catalytic properties of the transition elements probably arise on account of their capacity to give rise to various oxidation states and also of their capacity to form rather unstable intermediates, which decompose readily to form the product and regenerate the original catalyst.

Tendency towards complex formation : The transition metals in their various positive oxidation states, have great tendency to form complex ions or molecules with ligands, which are anions or neutral molecules having one or more lone-pairs of electrons. This tendency of the transition metal ions towards complex formation may be attributed to the following reasons :

(*a*) The transition metal cations are relatively small in size and hence, possess considerable positive charge-density. This makes them suitable *acceptor-centres*, capable of accepting the lone-pairs from the ligands or donors.

(*b*) The transition metal ions have vacant (n – 1) *d*-orbitals which possess the right amount of energy to accept and accommodate the lone-pairs from the donors.

The ligand-metal bonds in transition metal complexes are of the co-ordinate covalent type, in which both the bonding electrons are supplied by the donor. Because of the very small energy difference between the (n—1)*d*, n*s*- and n*p*-orbitals, they can undergo different types of hybridisations, leading to the formation of two, three, four, five and six energetically equivalent hybrid orbitals directed in definite directions in space and suitable for accommodating one, two, three, four, five or six lone-pairs respectively. Hence, transition metal complexes exhibit co-ordination numbers of two (linear), three (angular), four (tetrahedral and square planar), five (trigonal bipyramidal or square pyramidal) and six (octahedral).

Some important compounds of the transition metals (of the 1st transition series).

Oxides : The general formulae of the more well-known oxides of the 1st row transition metals are MO, M_2O_3, M_3O_4, MO_2, M_2O_5 and MO_3. Manganese forms a heptoxide of the formula Mn_2O_7.

The oxides of the metals in the low-valent state are basic and the oxides, in which the metal is in high oxidation state, are acidic. In general, the acidity of the oxides increase with the increase in positive oxidation state of the metal, the oxides of intermediate oxidation states being amphoteric. Thus, the oxides of the formula MO are distinctly basic and those with the formula MO_3 are definitely acidic. Most of the basic and the amphoteric oxides dissolve in non-oxidising acids to produce aquo-cations of the general formula $[M(H_2O)_6]^{n+}$.

The oxides of the formula MO_2 differ widely in their chemical properties. Thus, TiO_2 and MnO_2 are insoluble in water and dilute acids, while VO_2 easily dissolves in dilute acids. MnO_2 is acidic in character and produce manganate (MnO_4^{2-} ion, green) on fusion with an alkali peroxide or NaOH and KNO_3, which is converted into pink permanganate by the addition of acids (H^+).

Oxides of the type M_3O_4 are generally insoluble in acids but dissolve in them, as sulphates, after fusion with $KHSO_4$.

CrO_3 and Mn_2O_7 are highly acidic and dissolve in water forming acidic solutions and generating dichromate ($Cr_2O_7^{2-}$) and permanganate (MnO_4^-) ions.

Halides : The halides of the transition metals can be conveniently obtained by the following methods :

(*a*) By the direct reaction between the metal and the halogen. In this method the halides of the higher oxidation states of the metals are obtained : $2Fe+3Cl_2=FeCl_3$

(*b*) By heating a mixture of the metal oxide and carbon in an atmosphere (or current) of the halogen :

$$TiO_2+C+2Cl_2=TiCl_4+CO_2.$$

(*c*) By the reaction of the halogen hydracids (HF, HCl etc.) on metals or their basic and amphoteric oxides or carbonates. In this method the halides of lower oxidation states are obtained :

$$FeO+2HCl=FeCl_2+H_2O.$$

In a series of metals halides of the type MX_2 (say, MF_2, MCl_2, MBr_2 and MI_2), the ionic character of the M—X bond decreases as we go from fluorine to iodine. Thus, CuF_2 is an ionic solid but $CuCl_2$ and $CuBr_2$ are covalent solids, the former consisting of infinite chains of copper and chlorine atoms (see Vol. I, p. 415).

The halides hydrolyse in water, the ease of hydrolysis increasing with the increase in the oxidation state of the metal. Thus, $FeCl_3$ is much more hydrolysed in aqueous solution than $FeCl_2$.

This is due to the increase in the Lewis-acid character of the transition metal ion in the higher positive oxidation states.

Hydrides : Most of the transition metals form hydrides of the *interstitial type* (see Vol. I, p. 336-338). Generally, they adsorb hydrogen. In some cases, hydrogen is adsorbed at the surface at first, and then the hydrogen molecules dissociate into atoms and diffuse into the bulk of the metal to occupy interstitial positions. This is why many of them have variable compositions.

The nature of the M-H bond cannot be clearly defined and it probably represents an intermediate stage between ionic and covalent.

Sulphides: The sulphides of transition metals can be conveniently prepared by (i) the direct reaction of the metal and sulphur at elevated temperatures; (ii) by passing H_2S gas (or, by adding an aqueous solution of a soluble ionic sulphide like Na_2S) through a solution containing the metal ion at a suitable pH. Cu_2S and other sulphides of the low valent states may be prepared by reacting higher sulphides (like CuS) with elemental sulphur.

The transition metal sulphides are generally black or intensely coloured. They are insoluble in water and are polymeric in nature. *The heat of formation of the sulphides are less than those of the corresponding oxides and hence, they are less stable than the oxides.*

Carbides, borides and nitrides: At elevated temperatures, most of the transition metals react with the non-metals carbon, boron and nitrogen, forming the corresponding carbides, borides and nitrides. In most of these compounds, the small non-metal atoms occupy interstitial positions in the metal-lattices and hence, these are interstitial compounds.

INDIVIDUAL MEMBERS OF THE FIRST TRANSITION SERIES.

Now, we will briefly discuss the chemistry of the individual members of the first transition series. As the transition series starts from Gr. IIIA, such a discussion should begin from scandium. But, scandium is a rare element, finds very little practical use and is unfamiliar to us. For these reasons, we will leave scandium out and begin our discussion from the Gr. IVA member, **titanium.**

TITANIUM (Gr. IVA)

Occurrence: Titanium is fairly abundant and occurs in the earth's crust to the tune of $6 \times 10^{-1}\%$. However, the titanium-content of most of its minerals are too small to be commercially useful. The important ores from which titanium is extracted are the oxide ores, *rutile* (TiO_2) and *illmenite* ($FeTiO_3$).

Extraction of titanium.

By the Kroll process: Rutile or illmenite cannot be reduced to titanium by the carbon reduction process, as titanium (being a transition metal) forms carbide on heating with carbon, and nitride when heated in air. So, rutile or illmenite is converted to $TiCl_4$ at the first step by heating any one of them with carbon in a current of chlorine at 900°C :

$$TiO_2 + C + 2Cl_2 \overset{900°C}{=} TiCl_4 + CO_2\uparrow.$$

$TiCl_4$, being a volatile liquid boiling at 136°C, is vaporised and collected as a liquid in cooled vessels. It is then purified by fractional distillation.

Reduction of $TiCl_4$: The $TiCl_4$ vapour is then allowed to react with excess of powdered magnesium metal in a reduction furnace, maintained around 800°C, in an atmosphere of argon. $TiCl_4$ is reduced to metallic titanium and $MgCl_2$ is formed :

$$TiCl_4+2Mg=Ti+2MgCl_2.$$

Excess magnesium metal and $MgCl_2$ are distilled off in vacuum. Metallic titanium remaining in the reduction vessel is freed from residual Mg and $MgCl_2$ by leaching with dilute HCl. Metallic sodium may also be used in place of magnesium when the reaction, $TiCl_4+4Na=Ti+4NaCl$, takes place.

Titanium metal obtained by the Kroll process (named after the discoverer) is not very pure.

Purification of titanium metal by the **de-Boer Van Arkel or the hot-wire process :** Titanium obtained by the Kroll process is heated with iodine at about 200°C, when solid TiI_4 is formed. This titanium tetraiodide vapour is then allowed to enter an evacuated quartz bulb with a tungsten filament placed at its centre and electrically heated to ~1400°C. The TiI_4 vapour decomposes to the metal in contact with the hot filament and the metal is deposited on the filament, which grows thicker. Titanium metal is chipped off from the filament. This method produces titanium of very high purity.

Properties : Titanium is a hard, refractory metal with a density of 4.1, melting at 1668°C and boiling at 3260°C. It is a very strong metal with mechanical properties comparable to steel. Its technical importance is due to its lightness, mechanical strength and corrosion resistance. It is resistant to atmospheric corrosion because of the formation of a protective layer of oxide or nitride on its surface. It is a good conductor of heat and electricity.

At low temperatures, titanium is unreactive towards acids and alkalis due to the formation of a protective layer of oxide. At higher temperatures, it becomes much more reactive and reacts with boron, carbon, nitrogen, oxygen, the halogens. The boride, carbide and nitride are interestitial compounds, but are generally represented as TiB, TiC and TiN. Hot concentrated HCl and HNO_3 slowly dissolve the metal. The metal also dissolves in HF.

Uses : Titanium is used for hardening steel. It is used in the fabrication of jet engines, air-crafts, turbine engines and under-water equipments.

Electronic configuration : As already pointed out in the general discussion about the transition metals, titanium has the outermost electronic configuration of $3d^2 4s^2$. The two *ns*-electrons are paired up, while the two *d*-electrons are unpaired single electrons.

Oxidation states : Like all other transition metals, titanium exhibits variable oxidation states (see table 19.4) of +2, +3 and +4, corresponding to the removal of the two *ns*-electrons, two *ns* and one *d*-electron and two *ns* and two *d*-electrons respectively. Of these three oxidation states, the +4 state with d°-configuration, is the most stable.

Some important compounds of titanium.

Compounds of quadrivalent titanium, ***Ti (IV)*** **:**

Titanium dioxide, TiO_2 : It occurs in nature as rutile and is an important ore from which titanium is extracted. It can be obtained by boiling an aqueous solution of a titanium (IV) compound like $TiCl_4$: $TiCl_4+2H_2O=TiO_2\downarrow+4HCl$. This precipitate is strongly heated to get pure and dry TiO_2. It is a white lustrous powder, insoluble in water and acids. It is amphoteric in character. On fusion with alkalis and subsequent extraction with water, it goes into solution as titanates : $TiO_2+2NaOH=Na_2TiO_3+H_2O$. It goes into solution as titanium sulphate on fusion with $KHSO_4$ and subsequent extraction with 4-6 (N) H_2SO_4.

When mixed with carbon and heated in a current of chlorine, it forms $TiCl_4$.

It is used as a white pigment in cosmetics (like toilet soap, foundation lotions etc.) and also as a paint. As an outdoor paint, it is quite inert and has a good covering and coherent film-forming properties.

Titanium tetrachloride ($TiCl_4$) : It is generally obtained by heating a mixture of TiO_2 and carbon in a stream of Cl_2 gas : $TiO_2+C+2Cl_2=TiCl_4+CO_2\uparrow$.

It is a colourless fuming liquid which boils at 136°C. It is quickly hydrolysed by water in two steps. When water is present in small amounts, $TiOCl_2$ is produced : $TiCl_4+H_2O=TiOCl_2+2HCl$. In the presence of excess water, TiO_2 is precipitated : $TiCl_4+2H_2O=TiO_2\downarrow+4HCl$. $TiCl_4$ dissolves in concentrated HCl, forming halo-complexes of the type $[TiCl_6]^{2-}$ and $[Ti(H_2O)Cl_5]^-$. Because of the presence of the empty *d*-orbitals, $TiCl_4$ (and other halides) behaves as a strong Lewis acid towards oxygen donors like ethers, alcohols, esters etc. and forms adducts of the type $R_2O.\ TiCl_4$ and $(R_2O)_2.\ TiCl_4$.

Titanium tetrabromide and tetraiodide ($TiBr_4$ and TiI_4) : These can be conveniently prepared by heating the elements above 200°C in argon atmosphere. Both of these are crystalline solids with properties similar to $TiCl_4$.

Titanium sulphate, $Ti(SO_4)_2$: It can be prepared by fusing TiO_2 with $KHSO_4$ and extracting the melt with 6N H_2SO_4. On dilution with water $Ti(SO_4)_2$ is converted into $TiOSO_4$ first, and then to TiO_2.

Soluble titanium compounds can be reduced to the +3 state by zinc and dil HCl, zinc-amalgam (Jone's reductor) and cadmium-amalgam (cadmium reductor). It can be reduced to Ti^{+2} by electrolytic reduction.

Titanium (III) Compounds : Titanium (III) is a d^1-system, as it has lost three of its four valence-electrons.

Ti_2O_3 : It can be obtained by reducing TiO_2 with hydrogen at 1000°C : $2TiO_2+H_2=Ti_2O_3+H_2O$. It is quite stable and is not attacked by HCl or H_2SO_4. It is attacked by concentrated HNO_3.

Titanium trichloride, $TiCl_3$ (anhydrous) : This is obtained by passing a mixture of $TiCl_4$ vapour and hydrogen through a tube heated to 650−700°C : $2TiCl_4+H_2=TiCl_3+2HCl$. Anhydrous $TiCl_3$ is a violet powder which is easily oxidised to the +4 state. When dissolved in oxygen-free water, $TiCl_3$ (and most of the other soluble Ti^{+3} compounds) forms a blue-violet solution containing the hydrated titanium (III) ion, $[Ti(H_2O)_6]^{+3}$.

Titanium (III) hydroxide $Ti(OH)_3$: This can be obtained by treating a solution of a Ti(III) compound with a hydroxide, like NH_4OH : $TiCl_3+3NH_4OH=Ti(OH)_3\downarrow+3NH_4Cl$. On heating in an inert atmosphere, it is converted into Ti_2O_3. Other titamium (III) salts can be obtained by dissolving $Ti(OH)_3$ in the appropriate acids.

Titanium (III) compounds are strong reducing agents because of their tendency to go to the Ti(IV) state. Ti(III) reduces Fe^{+3} to Fe^{+2} : $Ti_2(SO_4)_3+Fe_2(SO_4)_3=2Ti(SO_4)_2+2FeSO_4$.

In general, titanium (III) compounds are more basic, and more ionic but less stable than the corresponding titanium (IV) compounds.

Titanium (II) Compounds : This +2 oxidation state arises due to the loss of the two 4*s*-electrons and is strongly reducing and highly unstable.

Titanium (II) Oxide, TiO : It is prepared by the reduction of the higher oxides with titanium metal. It is a non-stoichiometric compound with a titanium : oxygen ratio around 0·75. It has a great tendency to change into TiO_2 and hence, acts as a strong reducing agent. It is a basic oxide, strongly ionic in nature.

Other titanium (II) compounds : Other titanium (II) compounds can be obtained by the electrolytic reduction of the corresponding Ti (III) or Ti (IV) compound in aqueous acidic solutions. In this manner $TiCl_2$, $TiSO_4$ etc. can be obtained.

$TiCl_2$ is an ionic solid, strongly reducing in character. On heating, it disproportionates to Ti (IV) and Ti° :

$$2TiCl_2=TiCl_4+Ti.$$

Complex compounds of titanium : In the +4 state, titanium forms complexes mainly with oxygen and nitrogen donors. In many cases, titanium is present as the titanyl (TiO^{+2}) ion. Examples of complexes of Ti(IV) are K_2TiF_6 and $K_2TiO(C_2O_4)_2$—potassium hexafluoro titanate and potassium titanyl oxalate.

Titanium (III), a d^1-system, forms quite a number of complexes with oxygen, nitrogen and halogen donors. It forms both cationic (e.g. $[Ti(H_2O)_6]Cl_3$) and anionic (e.g. K_3TiF_6) complexes.

VANADIUM (Gr. VA).

Occurrence : Vanadium occurs widely in nature. Its extent of occurrence in the earth's crust is $2 \times 10^{-2}\%$ and hence, it is a fairly abundant element. It occurs in many minerals but, like titanium, very few minerals contain enough vanadium to make the extraction commercially utilisable.

The more important ores of vanadium are the sulphide ore *partonite* (mainly V_2S_5), *carnotite* [$K(UO_2)VO_4 . 3/2H_2O$], and *vanadinite* [$Pb_5(VO_4)_3Cl$]. Of these three, carnotite is primarlly an ore of uranium, but vanadium is also extracted from it.

Extraction : The extraction of pure vanadium metal from its ore is a difficult process because of its reactivity towards oxygen, nitrogen and carbon at the high temperatures generally used for the reduction processes. Pure vanadium is generally obtained from VCl_3 or VCl_4 by using excess of Na or Mg, through a process analogous to the Kroll process (employed for the extraction of titanium from $TiCl_4$) : $2VCl_3 + 6Na = 2V + 6NaCl$; $VCl_4 + 2Mg = V + 2MgCl_2$. Pure vanadim is also obtained from V_2O_5. In this process, V_2O_5 is heated with excess of calcium metal in a magnesite crucible, a small amount of iodine being added to the mixture. The function of iodine is to react with calcium, forming calcium iodide, and this reaction, being strongly exothermic, produces high temperature at which the reduction of V_2O_5 by calcium takes place : $V_2O_5 + 5Ca = 2V + 5CaO$.

Purification : Very pure vanadium can be obtained by the de-Boer-Van Arkel process described before in the case of titanium.

Properties : The pure metal is steel grey in colour and melts at $\sim 1700°C$. Presence of small amount of carbon markedly raises the m. p. It resembles titanium in being hard and corrosion resistant. It is a strong metal having good mechanical properties and is a good conductor of heat and electricity.

At room temperature, the metal is not attacked by air, moisture (or water), non-oxidising acid (except HF) and alkalis. However, it dissolvs in concenrated sulphuric acid, nitric acid and aqua regia. At elevated temperatures, it combines with non-metals like boron, carbon, nitrogen etc., forming boride, carbide and nitride respectively, all of which are interstitial compounds. In these reactions, it closely resembles titanium. On heating in air or oxygen, it produces V_2O_5 containing some lower oxides as impurities. When heated in a current of fluorine, it forms VF_5, but with chlorine it produces VCl_4 under similar conditions.

Uses : The principal uses of vanadium are in alloy steels and cast iron making to improve ductility, shock-resistance and corrosion resistance. Instead of pure vanadium metal, *ferrovanadium*, an alloy of iron and vanadium (containing 30-45% V) is generally used. In steel industry, it acts as a scavenger of oxygen and nitrogen and improves the mechanical properties of steel.

Manufacture of ferro-vanadium : Sodium vanadate, obtained by fusing vanadium ore with Na_2CO_3 and $NaNO_3$, is extracted with boiling water and the solution is treated with excess NH_4Cl. Ammonium metavanadate (NH_4VO_3) is precipitated as an orange solid. This is heated to produce brown V_2O_5 :

$$2NH_4VO_3 \xrightarrow{\text{heat}} V_2O_5 + 2NH_3 + H_2O.$$

This V_2O_5 is then mixed with iron oxide, carbon, a little fluorspar and heated in an electric furnance fitted with carbon electrodes, when ferro-vanadium is produced.

Electronic configuration : As already given in table 19.2, the valence-shell electronic configuration of vanadium is $3d^3\,4s^2$, in which the two $4s$-electrons are paired up, while the three d-electrons are in the unpaired condition.

Oxidation states : Like titanium (and all other transition metals), vanadium exhibits several oxidation states. The oxidation states of $+2$, $+3$, $+4$ and $+5$ corresponds to the removal (or involvement in bonding) of two $4s$, two $4s$ and one $3d$, two $4s$ and two $3d$ and two $4s$ and three $3d$-electrons (see Table 19.4). In the $+2$, $+3$ and $+4$ oxidation states, vanadium compounds are coloured and paramagnetic, because of the presence of three, two and one unpaired electrons, while in the $+5$ oxidation state, they are colourless and diamagnetic. When a colourless acidic solution of a V^{+5}–compound is treated with zinc dust, the colour first becomes blue, then green and finally violet due to the stepwise reduction of V^{+5} into V^{+4}, V^{+3} and V^{+2}.

Some important compounds of vanadium.

Compounds of vanadium (V) : This is the highest oxidation state of vanadium.

Vanadium pentoxide and Vanadates : Vanadium pentoxide, V_2O_5 may be obtained by burning powdered vanadium metal in excess oxygen : $4V+5O_2=2V_2O_5$. Commercially, it is prepared by heating ammonium metavanadate : $2NH_4VO_3=V_2O_5+2NH_3+H_2O$.

V_2O_5 is a brownish-orange powder melting around 650°C. It is very slightly soluble in water forming a pale yellow acidic solution. It is predominantly an acidic oxide and reacts with alkalies to produce vanadates : $2NaOH+V_2O_5 \rightarrow 2NaVO_3+H_2O$. However, it dissolves in non-oxidising acids to produce oxovanadium (IV) compounds: $V_2O_5+6HCl=2VOCl_2+Cl_2+3H_2O$. It is a strong oxidising agent which oxidises chloride to chlorine.

On heating with SO_2 it produces VO_2, and with hydrogen it yields V_2O_3.

Uses : In various oxidation reactions V_2O_5 is used as a catalyst. The most important of these is its use in the conversion of SO_2 to SO_3 by the contact process. It is widely used as an oxidising agent in organic chemistry for the oxidation of alcohols and many other compounds.

Halides and oxyhalides :

Vanadium pentafluoride, VF_5 : Only fluorine form the pentahalide, VF_5, when vanadium metal is strongly heated with fluorine : $2V+5F_2=2F_5$.

Vanadium oxytrichloride ($VOCl_3$) : It is best obtained by triturating V_2O_5 with anhydrous $AlCl_3$ in a dry atmosphere and distilling off the $VOCl_3$ formed in vacuum.

Vanadium oxytrifluoride (VOF_3) : It is prepared by the action of HF on $VOCl_3$: $VOCl_3+3HF=VOF_3+3HCl$.

These oxyhalides are covalent compounds, fuming strongly in moist air and is very rapidly hydrolysed by water, $VOCl_3$ being hydrolysed more quickly : $VOCl_3+2H_2O=HVO_3+3HCl$.

Compounds of Vanadium (IV). This is the stablest state of vanadium. The +5 state, in spite of its stable d° configuration is not so stable because of its strong oxidising character. Of the large number of compounds of vanadium (IV) we will disscuss only the most important ones like, VO_2, VX_4 and VOX_2 (X=halogens). In the +4 state vanadium acts a moderate oxidising agent.

Vanadium dioxide VO_2 : This may be obtained by reducing V_2O_5 by oxalic acid or SO_2. It is a crystalline solid, amphoteric in character and reacts with non-oxidising acid to produce vanadyl compounds : $VO_2+2HCl=VOCl_2+H_2O$; $VO_2+H_2SO_4=VOSO_4+H_2O$.

With alkalis it forms *vanadites* : $VO_2+2NaOH=Na_2VO_3+H_2O$.

Vanadium tetrachloride, VCl_4 : It can be obtained by passing dry chlorine over powdered vanadium metal or, ferrovanadium heated in a dry atmosphere in a quartz tube. The vapour of VCl_4 condenses in the cooled receiver as a deep brown liquid boiling at 154°C.

It is thermally unstable and decomposes to VCl_3 and Cl_2 on prolonged heating above its boiling point. It fumes in moist air and is rapidly hydrolysed to oxovanadium (IV) chloride or vanadyl chloride : $VCl_4+H_2O=VOCl_2+2HCl$.

Oxo-vanadium (IV) chloride or vanadyl chloride, $VOCl_2$:

As mentioned above, it may be obtained by the hydrolysis of VCl_4 or by heating V_2O_5 with HCl (see under V_2O_5). Pure $VOCl_2$ is obtained by heating pure $VOCl_3$ by metallic zinc. The pure compound is a green crystalline substance, extremely hygroscopic.

Oxovanadium (IV) sulphate or vanadyl sulphate, $VOSO_4$:

This is best obtained by heating a suspension of V_2O_5 in dilute H_2SO_4 to which ethyl alcohol is added from time to time. V_2O_5 is reduced to the VO^{+2} state and forms a deep blue solution. This solution on evaporation, yields beautiful blue crystals of $VOSO_4 \cdot 5H_2O$. On heating with concentrated H_2SO_4, it is converted into greyish-green anhydrous $VOSO_4$.

Compounds of vanadium (III) : In this state vanadium acts as a strong reducing agent. The vanadium (III) compounds are generally prepared by the reduction of compounds of the higher oxidation states of +5 or +4.

Vanadium (III) oxide, V_2O_3 : V_2O_3 is obtained by the reduction of V_2O_5 by heating with hydrogen at high temperatures : $V_2O_5+2H_2=V_2O_3+2H_2O$. It is a basic oxide and produces the hexaaquovanadium (III) ion, $[V(H_2O)_6]^{+3}$, on reaction with dilute non-oxidising acids.

Vanadium trichloride, VCl_3 : This is best obtained by heating V_2O_5 with sulphur monochloride (S_2Cl_2) at about 180°C. The product is extracted repeatedly with carbon disulphide to remove precipitated sulphur and excess of S_2Cl_2.

It is also obtained by reducing VCl_4 with hydrogen :

$$2VCl_4+H_2 = 2VCl_3+2HCl.$$

Anhydrous VCl_3 is obtained as a violet-pink crystalline solid, extremely hygroscopic in nature. It is easily hydrolysed by water.

Vanadium (III) sulphate, $V_2(SO_4)_3$: It is best obtained by the electrolytic reduction of V_2O_5 in sulphuric acid, until a green solution is produced. On concentration and subsequent cooling, this solution yields shining green needle shaped crystals of $V_2(SO_4)_3.H_2SO_4.12H_2O$. On heating at about 180°C this compound eliminates water and SO_3 and produces $V_2(SO_4)_3$ as a yellow powder.

Both VCl_3 and $V_2(SO_4)_3$ are powerful reducing agents.

Compounds of Vanadium (II) : Only a few compounds of Vanadium (II) are stable. All compounds of V^{+2} are very strong reducing agents due to their tendency to get oxidised to the +4 and +5 states.

Vanadium (II) oxide, VO : It may be obtained by heating V_2O_3 with vanadium metal at high temperatures and low pressures : $V_2O_3+V=3VO$. It is a strong reducing agent.

Vanadium (II) chloride, VCl_2 : When VCl_4 vapour mixed with hydrogen, is passed through a red-hot quartz tube, V^{+4} is reduced to V^{+2} by hydrogen :

$$VCl_4+H_2 = VCl_2+2HCl.$$

VCl_2 is a bright green crystalline solid, soluble in water forming a violet solution. The V^{+2} (vanadous) ion is a very strong reducing agent and reduces water to hydrogen gas. Thus, the violet solution of vanadous chloride evolves hydrogen and gradually turns green due to the formation of $[V(H_2O)_6]^{+3}$ ion.

Vanadium (II) sulphate, $VSO_4.7H_2O$: This is prepared by the electrolytic reduction of a sulphuric acid solution of V_2O_5 through which SO_2-gas is constantly bubbled. The solution is electrolysed until the colour changes to uniform violet.

It is fairly soluble in water and crystallises as red-violet monoclinic crystals of the formula $VSO_4.7H_2O$. This salt is isomorphous with $FeSO_4.7H_2O$ and forms double salts of the general formula $VSO_4.M_2SO_4.6H_2O$ ($M=NH_4^+$, Na^+, K^+) which are isomorphous with Mohr salt, $FeSO_4.(NH_4)_2SO_4.7H_2O$. These double salts are the stablest water soluble compounds of V^{+2}.

Complex compounds.

Complexes of Vanadium (V): Vanadium (V) halides and oxyhalides react with ammonium and alkali metal halides, to form halo-complexes :

$$VF_5+NaF = Na\,[VF_6]\,;$$
$$VOF_3+3NaF = Na_3\,[VOF_6].$$

Other complexes with oxygen donors and mixed oxygen-nitrogen donors are also well known.

Complexes of Vanadium (IV) : Vanadium tetrachloride, VCl_4, forms complexes of the general type VCl_4L_2 and VCl_4AA, where, L is a monodentate oxygen or nitrogen donor and A—A is a neutral bidentate donor molecule. These complexes are extremely susceptible to hydrolysis and form the corresponding oxovanadium (IV) species on contact with water : $VCl_4L_2+H_2O \rightarrow VOCl_2L_2+2HCl$. $VOCl_2$ and other oxovanadium (IV) compounds form large number of complexes with oxygen and nitrogen donors.

Complexes of Vanadium (III) : Vanadium (III) complexes are rather unstable in general. Anionic complexes of the type $[V(CN)_6]^{3-}$ and $[V(C_2O_4)_3]^{3-}$ are well known.

CHROMIUM

Chromium occurs to the extent of 0.037% of the earth's crust and hence, is a fairly abundant element. It occurs in concentrated deposits in the form of oxide ores. The only ore of chromium, from which chromium is profitably extracted, is the *chromite* or *chrome-iron ore*, $FeO.Cr_2O_3$ or $FeCr_2O_4$. It also occurs in nature as chrome ore (Cr_2O_3) and is also found as the lead chromate *crocoisite*, $PbCrO_4$. The countries where chromite ore is found in large quantities are, Turkey, South Africa and India.

Extraction of chromium : The following methods are used for the extraction of chromium.

(1) **Reduction of chromite by carbon:** Manufacture of *ferrochrome*. Powdered chromite ore is mixed with carbon plus a flux of lime and fluorspar and smelted in an electric furnace: $FeO.Cr_2O_3+4C\rightarrow 2Cr+Fe+4CO\uparrow$. The product obtained is called *ferrochrome* and generally contain ~ 75 chromium and ~ 4% carbon. Like *ferrovanadium* (see under vanadium), ferrochrome is widely used as the source of chromium in the manufacturing of special alloy steels.

(2) **Aluminothermic reduction of chromite ore:** At the first step chromite is converted into dry Cr_2O_3 in the following manner: The finely powdered chromite is intimately mixed with excess of Na_2CO_3 and a little CaO and roasted in a reverberatory furnace in presence of air, when Cr_2O_3 is oxidised and converted into the water soluble sodium chromate:

$$4FeO.Cr_2O_3+8Na_2CO_3+7O_2\rightarrow Na_2CrO_4+Fe_2O_3+8CO_2\uparrow.$$

The resultant mass is then treated with water and filtered. This concentrated solution contained all the Na_2CrO_4. This solution is then treated with calculated quantity of H_2SO_4 to convert sodium chromate to sodium dichromate:

$$2Na_2CrO_4+H_2SO_4\rightarrow Na_2Cr_2O_7+Na_2SO_4+H_2O.$$

It is now concentrated to the crystallisation point when the less soluble $Na_2SO_4.10H_2O$ crystallises out leaving $Na_2Cr_2O_7$ in solution*. This solution is further concentrated until crystals of $Na_2Cr_2O_7$ are obtained. This $Na_2Cr_2O_7$ can now be converted to Cr_2O_3 in two ways: (i) On heating with carbon, $Na_2Cr_2O_7$ is reduced to sodium chromite: $Na_2Cr_2O_7+3C\rightarrow Na_2Cr_2O_4+3CO\uparrow$. Sodium chromite, on treatment with water yields the precipitate of Cr_2O_3: $Na_2Cr_2O_4+H_2O\rightarrow Cr_2O_3\uparrow+2NaOH$. (ii) By heating $Na_2Cr_2O_7$ with NH_4Cl when, the ammonium dichromate formed in the first step is further decomposed into Cr_2O_3: $Na_2Cr_2O_7+2NH_4Cl=(NH_4)_2Cr_2O_7+2NaCl$; $(NH_4)_2Cr_2O_7\rightarrow Cr_2O_3+N_2+4H_2O$.

This Cr_2O_3 is dried, mixed with aluminium powder (in $Cr_2O_3:Al=3:1$ parts by weight) and packed in a refractory crucible which is kept embedded in sand to minimise heat loss by conduction. A charge of BaO_2 and magnesium powder is placed into the Cr_2O_3-Al mixture, which is ignited from outside by means of a magnesium ribbon. The reaction is first started by the heat generated by the burning of Mg-BaO_2 mixture, and once started, the tremendous heat evolved in the reduction of Cr_2O_3 by Al takes the reduction to completion : $Cr_2O_3+2Al=2Cr+Al_2O_3$ ($\triangle H=-112$ Kcal.), and this melts chromium (m.p.=1875°C), which collects at the bottom of the crucible. It is protected from oxidation by the layer of alumina floating above, and is taken out from a tap-hole at the bottom of the crucible. The metal obtained by this process is of ~ 92% purity. In many countries this process is replaced by one in which chromite is reduced by silicon instead of aluminium. This process is more economical and yields purer chromium.

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*This solution, after proper concentration and treatment with requisite quantities of KCl, yield crystalline precipitate of potassium dichromate, $K_2Cr_2O_7$ as this is much less soluble than $Na_2Cr_2O_7$. $(NH_4)_2Cr_2O_7$ can also be prepared by replacing KCl by NH_4Cl.

Apart from being the chief source of chromium metal, chromite is used for manufacturing refractory bricks of highest quality used for metallurgical purposes.

(3) **Electrolytic reduction of a Cr (III) salt in solution :**

A solution of $CrCl_3$ or $Cr_2(SO_4)_3$ (obtained from Cr_2O_3) is electrolysed with a mercury cathode and a lead anode. Pure chromium is deposited in the cathode and forms amalgam. This amalgam is heated in vacuo to distill off the mercury. This process yields chromium metal of 99.9% purity.

Properties : *Physical properties* : Chromium is a bluish-white metal, which melts at 1875°C. Pure chromium is rather soft, malleable and ductile. But, as it is almost invariably contaminated with carbon, it generally appears very hard. It takes a very high polish.

Chemical properties :

Action of air (O_2) and water : Except on heating in air or oxygen, chromium does not react with air under ordinary conditions. On heating with air or oxygen at a high temperature, it forms Cr_2O_3 : $4Cr+3O_2=2Cr_2O_3$.

It decomposes steam at red heat, but does not react with water under ordinary conditions :

$$2Cr+3H_2O=Cr_2O_3+3H_2\uparrow.$$

Action of acids : At room temperature, chromium is slowly attacked by dilute HCl and H_2SO_4, leading to the formation of blue-violet solutions of chromous [chromium (II)] salts :

$$Cr+H_2SO_4 = CrSO_4+H_2\uparrow \; ;$$
$$Cr+2HCl = CrCl_2+H_2\uparrow .$$

These blue chromous salts are extremely susceptible to oxidation by the oxygen of air and spontaneously change into the green chromic (III) salts :

$$4CrSO_4+2H_2SO_4+O_2=2Cr_2(SO_4)_3+2H_2O.$$

But hot, concentrated H_2SO_4 attacks chromium vigorously, forming chromic sulphate and liberating SO_2 :

$$2Cr+6H_2SO_4 = Cr_2(SO_4)_3+6H_2O+3SO_2\uparrow .$$

Dilute nitric acid has practically no action on chromium which becomes passive in concentrated nitric acid. This passivity arises out of the formation of a layer of insoluble oxide of chromium (III) on the surface of the metal.

Action of alkalis : The metal does not react with alkalis under ordinary conditions. It is not attacked by fused alkali in absence of air or any oxidising agent like a peroxide.

Action of halogens : On heating in a current of F_2 or Cl_2 (in absence of oxygen) chromium forms CrF_2 and $CrCl_2$.

Uses of chromium : The major and most important use of chromium is in the production of special alloy steels. Requisite quantity of chromium is added to molten steel in the form of *ferrochromium*, described before. The special steel, containing nickel ($\sim$10%) and chromium ($\sim$ 20%), is known as the *stainless steel.* This steel is highly resistant towards acids and many other chemicals.

Another very important use of chromium is in plating metals for the prevention of corrosion. For this purpose, chromium is electrolytically deposited in an uniform layer on the surface of the article. Alloys of nickel and chromium containing $\sim$ 20% chromium are used as resistance-type heating elements for heaters, electric furnaces etc. One such alloy is *nichrome* (Ni – 60%, Cr – 15% and Fe – 25%).

Electronic configuration and oxidation states : Coming after vanadium (valence-shell configuration $3d^3 4s^2$), chromium has rather unexpected valence-shell electronic configuration of $3d^5 4s^1$, the reason for which is already discussed (see vol. I, p. 99-100). From this valence-shell configuration, it appears that it may have any oxidation state from $+1$ to $+6$, corresponding to the participation of the requisite number of electrons in bonding. All these oxidation states are realised in practice, and along with them, a zero oxidation state is also achieved in its carbonyl compound, $Cr(CO)_6$. However, the oxidation states of $+1$, $+4$ and $+5$ are very unstable and are attained only in a few co-ordination complexes of chromium. The important oxidation states of chromium are $+2$, $+3$ and $+6$, of which the $+2$ state is quite unstable. *The chemistry of chromium is dominated by the $+3$ and $+6$ oxidation states.*

Compounds of Chromium.

Compounds of Chromium (II) : Halides : Chromous fluoride (CrF_2) and chromous chloride are obtained by passing F_2 or Cl_2 over red-hot chromium. CrF_2 is colourless and nearly insoluble. $CrCl_2$ can also be prepared by reducing $CrCl_3$ with hydrogen at high temperatures or by reducing dichromate by zinc amalgam and HCl :

$$K_2Cr_2O_7+6HCl+8[H] \rightarrow 2CrCl_2+2KCl+7H_2O.$$

From this solution, $CrCl_2$ may be obtained as a green dihydrate or a pale blue trihydrate. $CrBr_2$ and CrI_2, are also known and are similar to $CrCl_2$.

Chromous sulphate, $CrSO_4$: This is obtained by the same procedure adopted for the preparation of $CrCl_2$, using H_2SO_4 in place of HCl :

$$K_2Cr_2O_7+3H_2SO_4+8[H] \rightarrow 2CrSO_4+K_2SO_4+7H_2O.$$

[Addition of sodium acetate or sodium or ammonium oxalate to this solution of $CrSO_4$ (and also to a solution of $CrCl_2$), $Cr(CH_3COO)_2$ and CrC_2O_4 respectively, are obtained.] On crystallisation in absence of air or oxygen, bright blue crystals of the heptahydrate $CrSO_4.7H_2O$ are obtained. It is isomorphous with $FeSO_4$ and forms double salts (*schonites*) of the type $CrSO_4.(NH_4)_2SO_4.7H_2O$, which are isomorphous with Mohr salt.

All chromous compounds are strong reducing agents, which is evident from the E° value (-0.41 V) of the Cr^{+3}/Cr^{+2} system.

Chromium (III) compounds or chromic compounds.

Chromic oxide (chromium sesquioxide), Cr_2O_3 : This is obtained when $Cr(OH)_3$, $Cr(NO_3)_3$, or $Cr_2(SO_4)_3$ is ignited. It can also be obtained by heating ammonium dichromate :

$$(NH_4)_2Cr_2O_7 = Cr_2O_3+4H_2O+N_2\uparrow.$$

Cr_2O_3 is a stable green powder which is amphoteric in nature. Freshly prepared hydrated Cr_2O_3 dissolves in acids on heating to yield Cr (III) salts : $Cr_2O_3+6H^++3H_2O=2[Cr(H_2O)_6]^{+3}$.

It also dissolves in alkalis, forming chromites :

$$Cr_2O_3+2OH^- = \underset{\text{chromite ion}}{2CrO_2^{2-}}+H_2O.$$

When fused with an alkali in presence of air, it forms chromate : $2Cr_2O_3+8NaOH+3O_2 = 4Na_2CrO_4+4H_2O$. On ignition, chromium trioxide becomes insoluble in acids.

It dissolves in borax, producing green coloured metaborate :

$$Cr_2O_3+3Na_2B_4O_7 \rightarrow 2Cr(BO_2)_3+6NaBO_2.$$

Uses : The hydrated oxide $Cr_2O_3.2H_2O$ is used as a green pigment and goes by the name Guigret's green. It is also used in glass and porcelein industry to impart green colour to glass and porcelein articles.

Halides : All the halides, CrF_3, $CrCl_3$, $CrBr_3$ and CrI_3 are known. Of these, chromic chloride is of some importance.

Chromic chloride, $CrCl_3$: This is generally obtained by passing chlorine over a strongly heated mixture of Cr_2O_3 and carbon : $Cr_2O_3+3C+3Cl_2 = 2CrCl_3+3CO$. Anhydrous $CrCl_3$ is a pinkish-violet solid, almost insoluble in water. However, in presence of a trace of chromous salt, it readily dissolves, forming a green solution. It forms three soluble hexahydrates.

(i) The dark green α-variety, which is obtained by dissolving CrO_3 in concentrated HCl, evaporating the solution to crystallisation and finally cooling. On addition of $AgNO_3$ solution to a solution of this green α-variety, only one chloride ion is precipitated as AgCl. Hence, this variety has the structure $[Cr(H_2O)_4Cl_2]Cl.2H_2O$.

(ii) The violet β-variety is obtained by dissolving the α-variety in an equal weight of water, refluxing it for an hour, cooling in ice and passing HCl gas through this cold solution. On addition of $AgNO_3$ to a solution of this compound, all the three Cl^--ions are precipitated out as AgCl. It has the structure $[Cr(H_2O)_6]Cl_3$.

(iii) The light green γ-variety is obtained from the mother-liquor from the preparation of the β-variety, by adding ether saturated with HCl, and by passing HCl for some time, the temperature being kept near 10°C. Two Cl^--ions are precipitated as AgCl on the addition of $AgNO_3$ to a solution of this compound. Hence, its structure is $[Cr(H_2O)_5Cl]Cl_2 . H_2O$.

CrF_3, $CrBr_3$ and CrI_3 may be obtained as hexatydrates by dissolving $Cr(OH)_3$ in the respective acids and evaporating to crystallisation. These have properties similar to chromic chloride.

Chromic sulphate, $Cr_2(SO_4)_3$: This is best obtained by dissolving $Cr(OH)_3$ in hot concentrated H_2SO_4 and keeping the solution for a few weeks, when violet crystals are obtained. Two varieties of chromium (III) sulphate are known. The violet variety, $Cr_2(SO_4)_3 . 18H_2O$, is obtained as above, and the green variety, $Cr_2(SO_4)_3 . 6H_2O$, is obtained by heating the violet variety at 90°C until the composition corresponds to the formula $Cr_2(SO_4)_3 . 6H_2O$. The structure of the violet form is found to be $[Cr_2(H_2O)_{12}](SO_4)_3 . 6H_2O$ and that of the green variety is $[Cr_2(SO_4)_3(H_2O)_6]$

Double salts of Cr (III)—the Chrome alums [($M^1{}_2SO_4$, $Cr_2(SO_4)_3 . 24H_2O$] : Several double salts of Cr (III), having the general formula $M^1{}_2SO_4, Cr_2(SO_4)_3 . 24H_2O$ [where $M^1 = Na^+, K^+, NH_4^+$ etc.] are well-known. The most important of these is chrome alum, $K_2SO_4 . Cr_2(SO_4)_3 . 24H_2O$. This may be obtained by the reduction of a solution of $K_2Cr_2O_7$ in dilute H_2SO_4 on passing SO_2 through it :

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 = K_2SO_4 + Cr_2(SO_4)_3 + H_2O.$$

It is obtained as beautiful violet octahedral crystals. It is isomorphous with other alums like potash alum. It is highly soluble in water and forms a violet solution which turns green on heating above 60°C, due to the conversion of the $[Cr_2(H_2O)_{12}]^{+6}$ species to the green $[Cr_2(SO_4)_3(H_2O)_6]$ species.

Uses : It is used for tanning leather and in dyeing and calico-printing as a mordant.

Chromium (III) hydroxide, $Cr(OH)_3$: This is obtained by the addition of an alkali or NH_4OH to a solution of Cr(III) salt :

$CrCl_3+3NH_4OH=Cr(OH)_3\downarrow+3NH_4Cl$. It is precipitated as a dirty green gelatinous precipitate. It is an amphoteric substance and dissolves in acids, forming chromic salts and in alkalis to form chromites. On heating, it is converted into green Cr_2O_3.

Complexes of Cr(III) : Chromium (III) forms a large number of complexes with various mono-, bi- and polydentate donors. Some familiar examples of Cr(III) complexes are :
$[Cr(NH_3)_6]^{+3}$, $[Cr(H_2O)_6]^{+3}$, $[Cr(SCN)_6]^{3-}$, $[Cr(en)_3]^{+3}$, $[Cr(glycine)_3]^0$ etc. Most of the Cr(III) complexes have octahedral structure with a d^2sp^3-type of bonding.

CHROMIUM (VI) COMPOUNDS.

Chromium (VI) oxide or chromic anhydride, CrO_3 : This is obtained from $K_2Cr_2O_7$ by treatment with concentrated H_2SO_4 (or $HClO_4$) : $K_2Cr_2O_7+2H_2SO_4=2CrO_3\downarrow+2KHSO_4+H_2O$. On cooling, the orange-red crystals of CrO_3-separate out. CrO_3 is an orange-red crystalline solid. It volatilises at 110°C and melts at $\sim$190°C with partial decomposition. It is highly soluble in water, giving a highly acidic solution, which is supposed to contain several polychromic acids along with the monochromic acid, H_2CrO_4. The formation of the monochromic and polychromic acids may be represented as the addition of one mole of CrO_3 to the preceding one :

$$\begin{tikzcd}
H_2O \arrow[r, "CrO_3"] & \underset{\text{monochromic acid}}{H_2CrO_4} \arrow[r, "CrO_3"] & \underset{\text{dichromic acid}}{H_2Cr_2O_7} \arrow[r, "CrO_3"] & \underset{\text{trichromic acid}}{H_2Cr_3O_{10}} \arrow[d, "CrO_3"] \\
& & \text{etc.} & \underset{\text{(tetrachromic acid)}}{H_2Cr_4O_{13}} \arrow[l]
\end{tikzcd}$$

These polychromic acids have never been isolated in pure state and are rather unstable even in solution. However, their salts are known.

CrO_3 is a powerful oxidising agent and oxidises many organic compounds like alcohols, aldehydes, ketones, acids, sugars etc. In acid medium, it also oxidises many inorganic compounds such as ferrous salts, stannous salts, iodide, SO_2, H_2S etc. In each case, the

Cr(VI) is reduced to the Cr(III)-state. As these oxidation reactions are identical with those of the dichromates, they are discussed under the dichromates.

Chromates : Chromates, like sodium and potassium chromates can be conveniently prepared by dissolving CrO_3 in NaOH or KOH solutions : $CrO_3+2NaOH=Na_2CrO_4+H_2O$.

However, Na_2CrO_4 and K_2CrO_4 are obtained commercially from dichromates by treatment with calculated amounts of Na_2CO_3 or K_2CO_3 to the solutions of $Na_2Cr_2O_7$ and $K_2Cr_2O_7$ respectively : $Na_2Cr_2O_7+Na_2CO_3=2Na_2CrO_4+CO_2$; $K_2Cr_2O_7+K_2CO_3=2K_2CrO_4+CO_2$.

These solutions, on evaporation and cooling, yield lemon-yellow crystals of $Na_2CrO_4.H_2O$ and K_2CrO_4. The dichromates ($Na_2Cr_2O_7$ and $K_2Cr_2O_7$) are manufactured from the chromite ore by the usuál procedure. On treatment with an acid, yellow chromates are converted into the orange dichromates :

$$2K_2CrO_4+2H^+=K_2Cr_2O_7+2K^++H_2O.$$

Dichromates : The dichromates can easily be obtained by the acidification of chromate solutions and subsequent evaporation and crystallisation. However, $Na_2Cr_2O_7$ and $K_2Cr_2O_7$ are comercially obtained from chromite ore by the process underlined in the first portion of the aluminothermic process of extraction of chromium from chromite ore (see p. 3]9).

Potassium dichromate, $K_2Cr_2O_7$: This is the most important dichromate, as it is obtained in extremely pure condition and is highly stable under ordinary conditions. It occurs as orange-red crystals, melting at 398°C. It is fairly soluble in cold water and highly soluble in hot water.

On strong heating, it is decomposed into Cr_2O_3 and chromate, evolving oxygen : $4K_2Cr_2O_7=2Cr_2O_3+4K_2CrO_4+3O_2\uparrow$.

When heated with an ionic chloride and conc. H_2SO_4, it gives off the red-brown vapours of chromyl chloride, CrO_2Cl_2 :

$$K_2Cr_2O_7+4NaCl+6H_2SO_4$$
$$=2CrO_2Cl_2\uparrow+2KHSO_4+4NaHSO_4+3H_2O\ ;$$

Or,

$$Cr_2O_7{}^{2-}+4Cl^-+6H^+ \quad =2CrO_2Cl_2\uparrow+3H_2O.$$

This reaction is utilised for the detection of chloride in a sample.

[*This reaction requires the presence of* Cl^- *ions and hence, chlorides like* $HgCl_2$, Hg_2Cl_2 *and* $SnCl_2$, *which posses much covalent character, do not respond to this chromyl chloride test.*]

Like all the dichromates, $K_2Cr_2O_7$ is a powerful oxidising agent and oxidises many organic and inorganic compounds. E° value of the system, $Cr_2O_7^{2-}+14H^++6e \rightarrow 2Cr^{+3}+7H_2O$, is 1.36 volts at 25°C. This indicates that, in acid solution dichromate is as strong an oxidant as chlorine (E° of $\frac{1}{2}$ $Cl_2+e \rightarrow Cl^-=1.36$ volts at 25°C). Several oxidation reactions, involving the dichromate ion, are included in Chapter VI, vol. I, p. 253-254.

We have already noted that on treatment with an alkali, a dichromate is converted into a chromate and on acidification a chromate changes over to a dichromate :

$$Cr_2O_7^{2-}+2OH^-=2CrO_4^{2-}+H_2O\ ;$$
$$2CrO_4^{2-}+2H^+\quad=Cr_2O_7^{2-}+H_2O.$$

In an aqueous solution of a dichromate, the following equilibrium is immediatily established :

$$Cr_2O_7^{2-}+H_2O \rightleftharpoons 2HCrO_4^- \rightleftharpoons 2H^++2CrO_4^{2-}.$$

On the addition of a base, the proton of $HCrO_4^-$ ion is neutralised and $HCrO_4^-$ is removed as CrO_4^{2-} and hence, according to the Le Chatalier's principle, the equilibrium shifts to the right and more and more chromate is produced. On addition of an acid, the concentration of H^+ increases and gradually forces the equilibrium to the left, towards the formation of the $Cr_2O_7^{2-}$ ion.

Uses : $K_2Cr_2O_7$ is used as a primary standard oxidant for volumetric analysis of many reducing agents like ferrous iron, iodide etc. It is used in leather tanning, and in dyeing and calico-printing. It is also used for the preparation of several important chromium compounds like chrome alum, chrome yellow ($PbCrO_4$, used as a pigment), chrome red ($PbO.\ PbCrO_4$, also used as a pigment), zinc yellow ($ZnCrO_4$, which is also used as a pigment). Mixed with concentrated H_2SO_4, it is widely used by the organic chemists as a powerful oxidant.

Chromyl chloride, CrO_2Cl_2 : As already pointed out under potassium dichromate, chromyl chloride is prepared by distilling a mixture of $K_2Cr_2O_7$, an ionic chloride and concentrated H_2SO_4, when CrO_2Cl_2 distils over as a dark-red liquid. It boils at 116°C. It is rapidly hydrolysed by water or an alkali, forming chromate :

$$CrO_2Cl_2+4NaOH=Na_2CrO_4+2NaCl+2H_2O.$$

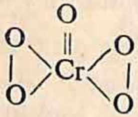
[*It may be pointed out here that, if a bromide or an iodide is treated in a similar manner, chromyl bromide and iodide are not formed. Hence, this test may be utilised for the detection of chloride in presence of bromide and iodide.*]

CrO_2Cl_2 is a very powerful oxidising agent and reacts with burning sulphur, phosphorus, ammonia and a large number of organic compounds with explosive violence. It is used in organic chemistry for the oxidation of a methyl group attached to an aromatic ring to the corresponding aldehyde.

Chromium peroxide, CrO_5 : When the solution of a chromate or dichromate is acidified with H_2SO_4 and shaken with H_2O_2, a transient deep-blue colour is observed. If some ether or amyl alcohol is added to the solution prior to the addition of H_2O_2, this blue colour is extracted into the upper ether or amyl alcohol layer and remains stable for quite a long time. Formerly, it was thought that this blue colour is due to the formation of a perchromic acid, variously described as $HCrO_5$, H_3CrO_8 etc. But, now it has been established that this is chromium peroxide, CrO_5 :

$$CrO_4^{2-}+2H^++2H_2O_2=\underset{\text{blue}}{CrO_5}+3H_2O.$$

The structure of CrO_5 is represented as follows :



Some other chromium compounds of industrial importance :

Chrome yellow ($PbCrO_4$) : It is obtained by the addition of a solution of $Na_2Cr_2O_7$ to an aqueous solution of lead nitrate or lead acetate. It has a bright-yellow colour and is used as a pigment.

Chrome green : This is obtained by thoroughly mixing finely pulverized chrome yellow with prussiun blue, $Fe_4[Fe(CN)_6]_3$. This is also used as a pigment.

Chrome red or basic lead chromate, $PbO.PbCrO_4$: It is obtained from chrome yellow, by digesting it with a dilute solution of NaOH. It is a brilliant-red powder and is used as a pigment, either alone or mixed with $PbCrO_4$.

Zinc yellow or basic zinc chromate, $(Zn(OH)_2ZnCrO_4.H_2O$: This also is a yellow pigment which is prepared by treating a neutral zinc salt solution with K_2CrO_4.

Guigret's green or hydrated chromic oxide, $Cr_2O_3.2H_2O$: This is manufactured by fusing $K_2Cr_2O_7$ and boric acid in equimolecular proportions. It is a bright-green powder, widely used as an inert outdoor pigment.

MANGANESE (Gr. VII A)

Manganese occurs in Group VII A of the periodic table, along with technetium and rhenium. With an atomic number of 25, it possesses the valence-shell electronic configuration, $3d^5 4s^2$. The difference in the properties of the members of the two sub-groups reaches maximum in Group VII of the periodic table and hence, we find that manganese of Group VIIA differs widely from the halogens. the elements of Group VIIB. It will be seen from the electronic configuration of the manganese atom that it is a transitional element belonging to *d-block*, while the halogens are representative elements. Besides, manganese is a typical metal (electropositive element), while the halogens are strongly electronegative non-metals. But, below these dissimilarities, there lie certain resemblances between manganese and some of the halogens. Such resemblances are, however, restricted to the highest oxide (Mn_2O_7) of manganese and its derivatives on the one hand, and Cl_2O_7 and its derivatives on the other. In these highest oxides and their derivatives, both Mn and Cl exhibit their group-valency of 7 and their octet is fully shared. Mn_2O_7 and Cl_2O_7 are both acidic, volatile and explosive in nature. Permanganic acid ($HMnO_4$) and perchloric acid ($HClO_4$) are analogous and very strong acids. Potassium permanganate and potassium perchlorate are isomorphous salts. Again, both silver permanganate and silver perchlorate are sparingly soluble in water. All these similarities somewhat justify the placement of manganese with the halogens in the same group (Group VII) of the periodic table. But, once the compounds of Mn and Cl in their reduced state are compared, the above similarities disappear altogether. Thus, chlorine is electronegative in its compounds devoid of oxygen, and manganese in lower oxidation states is completely basigenic and exhibits close similarities with its neighbours like chromium and iron, which will be discussed later.

Occurrence : Manganese is a relatively abundant metal and constitutes about 0·085% of earth's crust. Although widely distributed in nature, the metal occurs in certain substantial deposits of good ores, the most important of which is **pyrolusite** (impure MnO_2, containing 60-63% MnO_2). It is found in large quantities in India, U.S.S.R., Africa, Brazil and Chile. [In fact, India is the largest producer of pyrolusite in the world. The ore is chiefly available in Orissa, Madhyapradesh, Bihar, Maharastra and Karnatak.] Other important ores of manganese are : **Braunite** (Mn_2O_3), **Manganite** [$MnO(OH)$], **Hausmanite** (Mn_3O_4), **Manganese spar** ($MnCO_3$) and **Manganese blende** (MnS). The metal is associated with many iron ores. Plant and animal cells contain trace amounts of manganese, which is essential for important biological processes.

Extraction ; Pyrolusite is the chief source material for the extraction of manganese, and it is generally extracted by the thermit process. But, as MnO_2 itself reacts violently with powdered aluminium at high temperatures, it is first converted to Mn_3O_4 by strongly heating in air before reduction. The finely powdered and heated ore is freed from the associated iron oxide by electromagnetic separation. It is then intimately mixed with aluminium powder (a slightly less amount than the theoretical quantity of Al-powder is generally employed) and some fluorspar, and the mixture is subjected to the thermit process (see vol. I, p. 524) : $3MnO_2 = Mn_3O_4 + O_2$; $3Mn_3O_4 + 8Al = 9Mn + 4Al_2O_3$.

[Aluminium oxide, obtained as the by-product in the above metallurgy, is artificial *corundum* which is generally used as an abrasive or for polishing purposes.]

Manganese in the pure state, can be prepared by the electrodeposition from an acidified solution of manganese ammonium sulphate, using lead anodes and stainless steel cathodes.

Properties : Manganese is silvery-white, hard and brittle. It has a density of 7·1, melts at 1247°C and boils at 1900°C. In the pure state, it is stable in air ; but, when the finely divided metal is heated in air, it is oxidised and sometimes catches fire. Water is also decomposed by the finely divided metal, especially in the presence of NH_4Cl which prevents the formation of insoluble coating of manganous hydroxide on the metal surface. It readily dissolves in dilute mineral acids, with the evolution of hydrogen : $Mn+2HCl = MnCl_2+H_2\uparrow$. Boiling conc. H_2SO_4 and HNO_3 dissolves the metal with the evolution of SO_2 and nitric oxide respectively. The metal combines directly with the halogens, sulphur and phosphorus at moderate heat, and with nitrogen at high temperature to form the respective binary compounds. Manganese forms alloys with many metals. Those with iron, known as *ferromanganese* and *spiegeleisen*, are of much technical importance in steel industry. The metal is paramagnetic.

Uses : Manganese is largely used in steel industry in the form of ferromanganese or spiegeleisen. When added in small quantities, it removes traces of sulphur and oxygen from steel ; and in larger quantities, it forms very tough alloy-steel (manganese steel). Among the non-ferrous alloys of manganese, the most important ones are : (i) *manganese bronze* (containing copper with varying amounts of Mn and Zn), (ii) *manganin* (83% Cu, 13% Mn ; 4% Ni ; used for making resistance coils), (iii) *Heussler's* alloy, a ferromagnetic alloy of Cu, Al and Mn.

[Ferromanganese and spiegeleisen are manufactured by smelting a mixture of of iron and manganese ores in the blast furnace. Ferromanganese contains 30-80% Mn (with less than 0·3% carbon) and spiegeleisen contains 5-20% Mn (with more than 0·3% carbon.)]

COMPOUNDS OF MANGANESE.

Oxidation states of manganese : It is evident from the electronic configuration of the manganese atom that, it should exhibit a maximum oxidation state of +7. This is no doubt, true ; but, the metal is also known to exist in various lower oxidation states. In fact, manganese compounds, containing the metal in −3, −1, 0, +1, +2, +3, +4, +5, +6 and +7 are all known. This is why (as already mentioned in the general discussion about the transition elements), manganese is marked as *the most versatile element of the periodic table.* Of these, the compounds having the metal in the +2 and +7 oxidation states are most common and stable. It should, however, be mentioned that some of the unstable oxidation states of manganese may be more or less stabilised by complex formation. [The compounds of manganese in −3, −1, 0 and +1 oxidation states of the metal are generally unstable and highly reducing substances, and are mostly complex carbonyls, nitrosyls, cyanides *etc.*]. The +2 oxidation state of the metal is the most stable one (which is due partly to the *half-filled shell* of Mn^{II}) ; but it is quite readily oxidised in alkaline medium. The chemistry of Mn^{III} is not extensive and in aqueous solution, it is quite unstable, being readily reduced to Mn^{II}. In aqueous solution, Mn^{III} disproportionates into Mn^{II} and Mn^{IV} :

$$2Mn^{+3}+2H_2O=Mn^{+2}+MnO_2\,(s)\downarrow+4H^+.$$

The chemistry of Mn^{IV} is not also extensive. Mn^{IV} is stable only in complex ions such as $[MnF_6]^{2-}$ and in MnO_2. The +5 oxidation state of manganese is very uncommon. Mn^{VI} is fairly stable as the manganate ion, $[MnO_4]^{2-}$ only in very basic solution ; but, in acid, neutral or slightly basic solutions, it readily disproportionates as follows :

$$3MnO_4^{2-}+4H^+=MnO_2+2MnO_4^-+2H_2O.$$

Mn^{VII} is best known as the more or less stable permanganates, the salts of $[MnO_4]^-$ ion. Mn_2O_7 (an oily liquid) is stable only below 0°C.

Compounds of Mn (II).

Manganous oxide (MnO) is a dull green powder and is obtained by the thermal decomposition of manganous carbonate or manganous oxalate and also by strongly heating other higher oxides of the metal in a current of hydrogen gas : $MnCO_3=MnO+CO_2$; $MnC_2O_4=MnO+CO\uparrow+CO_2$; $MnO_2+H_2=MnO+H_2O$. The oxide dissolves in acids to form manganous salts.

Manganous hydroxide, $[Mn(OH)_2]$, is thrown down as a white precipitate by the treatment of Mn(II) salt solutions with alkali hydroxides. The white precipitate readily turns brown on exposure to air due to oxidation into manganic hydroxide, MnO(OH).

Manganous hydroxide is incompletely precipitated by NH_4OH, and it may not be precipitated at all by NH_4OH in presence of NH_4Cl. This is due to the fact that, in the latter case, the concentration of OH^- ions is rather small as compared to what is required to exceed the solubility product of $Mn(OH)_2$ ($K_{sp}=[Mn^{++}][OH^-]^2=\sim10^{-12}$), and also the much lowering of $[Mn^{++}]$ through complex formation with ammonia.

Manganous halides, MnX_2 (X=F, Cl, Br and I).

Manganous chloride ($MnCl_2$) is the most important member of Mn(II) halides. It is prepared in the anhydrous state by the action of dry HCl gas on MnO, $MnCO_3$ or the metal itself, and also by burning the powdered metal in dry chlorine gas. The hydrated salt is formed with 2, 4 or 6 molecules of water of crystallisation. Among these, the tetrahydrate, $MnCl_2.4H_2O$, is common and is obtained by dissolving $MnCO_3$ in dilute HCl and concentrating the solution below 60°C. The hexahydrate, $MnCl_2.6H_2O$, is formed on crystallising the solution at lower temperatures and the dihydrate, $MnCl_2$, $2H_2O$, at higher temperatures. The dihydrate becomes anhydrous on heating at 98°C.

The tetrahydrate can also be prepared by strongly heating powdered **pyrolusite** with ammonium chloride in a crucible and extracting the residue with boiling water. The filtered aqueous extract gives the product on evaporation :

$$3MnO_2+6NH_4Cl=3MnCl_2+N_2\uparrow+4NH_3\uparrow+6H_2O\uparrow.$$

The anhydrous manganous chloride forms rose-red deliquescent crystals, while the crystals of the hydrated salts are pale pink in colour. It is highly soluble in water and forms double salts of the compositions $M^ICl.MnCl_2$, $2M^ICl.MnCl_2$ *etc.*, where M^I=an alkali metal.

Manganese bromide and iodide ($MnBr_2$ and MnI_2) are similar to the chloride in appearance and properties. But, the capacity of forming double salts is much weaker for the bromide and is practically nil for the iodide.

Manganous carbonate ($MnCO_3$) occurs in nature as *manganese spar*. It can be prepared as a white substance by adding $NaHCO_3$ solution to a manganous salt solution. The compound is somewhat soluble in water saturated with CO_2, due to the formation of soluble manganous bicarbonate, $Mn(HCO_3)_2$. Manganous carbonate is changed into $Mn(OH)_2$ on boiling with water, and CO_2 is liberated during this change. On gentle heating, the solid salt decomposes into MnO and CO_2.

Manganous nitrate, $Mn(NO_3)_2.6H_2O$ is the most important hydrate of the salt (several other hydrates are also known) and is prepared as pink deliquescent crystals on evaporating the solution obtained by dissolving $MnCO_3$ in slight excess of dilute HNO_3. The anhydrous salt may be obtained by warming the hydrated salt with conc. HNO_3. The solid salt decomposes on heating : $Mn(NO_3)_2=MnO_2+2NO_2\uparrow$.

Manganous phosphate, $Mn_3(PO_4)_2.7H_2O$: When a solution of a manganous salt is treated with excess of Na_2HPO_4 solution, the white precipitate of the heptahydrate is formed. When the above precipitation is carried out in ammoniacal medium in presence of NH_4Cl, pinkish white crystalline precipitate of **manganous ammonium phosphate** is thrown down quantitatively. The precipitate, after drying at 110°C, conforms to the composition $MnNH_4PO_4.H_2O$, which is transformed into manganous pyrophosphate, $Mn_2P_2O_7$, on ignition : $2MnNH_4PO_4=Mn_2P_4O_7+2NH_3\uparrow+H_2O\uparrow$. This serves as the basis of the gravimetric estimation of manganese.

Manganous sulphide (MnS) : On passing H_2S gas through a solution of manganous salt, containing NH_4OH and NH_4Cl, a flesh-coloured amorphous precipitate of manganous sulphide is obtained. It is the metastable form of the compound which is transformed into the stable, green crystalline variety on heating at 300°C in a current of H_2S, or on boiling with yellow ammonium sulphide solution. Manganous sulphide is soluble in acids.

Manganous sulphate ($MnSO_4$) : This salt is prepared by heating powdered pyrolusite with conc. H_2SO_4, evaporating the liquid and then gently igniting the residue to decompose ferric sulphate that is formed from the oxides of iron contained in pyrolusite. Manganous sulphate remains unaffected by this procedure, and is extracted with water. The filtered aqueous extract, on evaporation, yields pink efflorescent crystals of the tetrahydrate, $MnSO_4.4H_2O$. Several other hydrates of manganous sulphate are known. When the crystallisation of a $MnSO_4$ solution is carried out at temperatures below 9°C, the heptahydrate, $MnSO_4.7H_2O$, isomorphous with $FeSO_4.7H_2O$ (*green vitriol*) is formed. Between 9°–27°C, the crystallisation produces the pentahydrate, $MnSO_4.5H_2O$, isomorphous with $CuSO_4.5H_2O$ (*blue vitriol*). When the hydrated salts are heated at about 280°C, the colourless anhydrous salt is formed. [Manganese is sometimes estimated gravimetrically by weighing as the anhydrous sulphate.] Manganous sulphate forms crystalline double salts with ammonium sulphate or alkali metal sulphates, such as $K_2Mn(SO_4)_2.6H_2O$, $(NH_4)_2Mn(SO_4)_2\,6H_2O$ which are isomorphous with Mohr's salt.

Compounds of Manganese (III) : Manganese (III) or *manganic* salts are powerful oxidising agents. They are readily hydrolysed in water with the formation of Mn(II) salts and separation of MnO_2 :

$$2Mn^{+++}+2H_2O=Mn^{++}+MnO_2\downarrow+4H^+.$$

Thus, the solutions of manganic salts are acidic due to hydrolysis and as such, they are stable in strong acidic solutions. Complex manganic salts are, however, quite stable.

Manganic oxide and hydroxide [Mn_2O_3 and $MnO(OH)$] : Manganic oxide (Mn_2O_3) occurs as the ore *braunite*. It can be artificially prepared as a brown powder by heating MnO or MnO_2 in air to redness (550 – 950°C). On heating above 950°C, Mn_2O_3 loses oxygen and forms Mn_3O_4.

Manganic hydroxide, MnO(OH), is obtained as a brown powder, when Cl_2 gas is passed through a suspension of $MnCO_3$ in water or sodium carbonate solution ; the excess $MnCO_3$, if any, is removed by dissolving it out with very dilute nitric acid :

$$3MnCO_3+Cl_2+H_2O=2MnO(OH)+MnCl_2+3CO_2\uparrow.$$

Dilute hydrofluoric acid and concentrated H_2SO_4 and H_3PO_4 dissolve both Mn_2O_3 and MnO(OH) to produce manganic fluoride, manganic sulphate and manganic phosphate respectively. These two compounds are, therefore, believed to contain tervalent manganese, with the molecular constitution, $O=Mn-O-Mn=O$ and $O=Mn-OH$ respectively. But, as they react with hot, dilute HNO_3 to produce manganous nitrate and manganese dioxide ($Mn_2O_3+2HNO_3=Mn(NO_3)_2+MnO_2+H_2O$), manganic oxide is often regarded as the mixed oxide, $MnO.MnO_2$, or manganous manganite $Mn^{II}(Mn^{IV}O_3)$. But, the tervalency of the metal in these two compounds is more widely accepted.

An artificially prepared manganic hydrate, known as *manganese brown*, used as a brown-black pigment in cloth dyeing and printing, is prepared by treating $MnCl_2$ solution with bleaching powder and lime water.

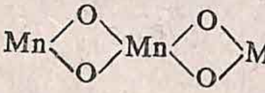
Mangano-manganic oxide, Mn_3O_4, occurs in nature as the mineral *hausmannite*. It is the most stable oxide of manganese, and is obtained as a brownish-red powder by igniting any other oxide of the metal above 950°C. [Manganese is sometimes estimated by by weighing as Mn_3O_4.] The oxide dissolves slowly in cold concentrated H_2SO_4 to form a red solution containing both manganous and manganic sulphates :

$$Mn_3O_4 + 4H_2SO_4 = MnSO_4 + Mn_2(SO_4)_3 + 4H_2O.$$

It, therefore, behaves as an equimolecular mixture of manganous and manganic oxide (MnO, Mn_2O_3). But, its reaction with boiling HNO_3, producing manganous nitrate and manganese dioxide,

$$[Mn_3O_4 + 4HNO_3 = 2Mn(NO_3)_2 + MnO_2 + 2H_2O],$$

suggests its formulation as the mixed oxide of bivalent and tetravalent manganese, *viz*. $2MnO.MnO_2$, or as manganous manganate, $Mn_2^{II}(Mn^{IV}O_4)$, or basic manganous manganite, $MnO^{II}(Mn^{IV}O_3)$, of the constitution



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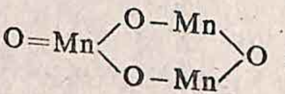


respectively.

Manganic halides : Manganic fluoride ($MnF_3.3H_2O$) has been isolated in the solid state ; manganic chloride ($MnCl_3$) is too unstable to be isolated as a solid, but it is known in solution ; manganic bromide and iodide are not known.

Manganic fluoride ($MnF_3.3H_2O$) is obtained as deep red crystals by dissolving Mn_2O_3 in hydrofluoric acid solution, or by oxidising manganous salts with potassium permanganate in hydrofluoric acid medium. In both the cases, the resultant solution is filtered and concentrated to obtain the crystals of $MnF_3.3H_2O$. The compound is decomposed on heating into manganous fluoride and fluorine : $2MnF_3 = 2MnF_2 + F_2$. It forms complex fluorides of the type $K_2MnF_5.H_2O$ with alkali metal fluorides.

Manganic chloride ($MnCl_3$) : When manganese dioxide is dissolved in cold conc. HCl, a deep brown solution is obtained, and it contains manganic chloride. When solid KCl is added to the above brown solution and HCl gas is passed into it in the cold till it is saturated with the gas, the dark red complex salt, K_2MnCl_5, separates out. But, pure $MnCl_3$ cannot be isolated from the above solution.

Manganic sulphate, $Mn_2(SO_4)_3$: It is obtained as a dark-green precipitate on cooling a solution of precipitated manganese dioxide in conc. H_2SO_4. The precipitate is filtered, washed with conc. HNO_3 and dried at 150°C. Manganic sulphate forms deliquescent powder, soluble in water to form a violet coloured solution. The solution gives a precipitate of manganic hydroxide on dilution. It forms violet coloured double sulphates or *alums* with alkali metal sulphates and ammonium sulphate, and they are isomorphous with potash alum, ferric alum and chrome alum. Except the cesium manganic alum, the other manganic alums are more or less hydrolysed in aqueous solutions to form hydrated manganic oxide.

Manganic phosphate : Several phosphates of tervalent manganese are known. Among them, the *orthophosphate*, $MnPO_4.H_2O$, is green ; the *metaphosphate*, $Mn(PO_3)_3$ is red and the others are violet—all being insoluble in water. [The violet colour of the microcosmic salt bead, formed in the oxidising flame by manganese compounds, is due to the formation of Mn (III) phosphate.] Violet manganese (III) phosphate is specially prepared for use as a permanent violet pigment in artists' work.

Compounds of manganese (IV).

Manganese dioxide (MnO_2) is the most familiar and important compound of manganese (IV), and it occurs widely as *pyrolusite*, the chief ore of the metal. It is difficult to obtain pure MnO_2 from pyrolusite and as such, the pure material is prepared artificially by heating manganous nitrate :

$$Mn(NO_3)_2 = MnO_2 + 2NO_2 \uparrow .$$

Hydrated manganese dioxide is obtained as a brownish black precipitate during the reduction of manganates or permaganates in alkaline medium, or by the oxidation of Mn (II) salts with bleaching powder.

Anhydrous MnO_2 is greyish-black to black crystalline powder, insoluble in water and dilute acids. It loses oxygen on heating above 530°C, forming Mn_2O_3 first and then Mn_3O_4. The oxide is amphoteric. As a feebly acidic oxide, it combines with strong bases to form manganites (*e.g.* $CaMnO_3$), and as a basic oxide, it reacts with cold concentrated hydrochloric acid to form a dark brown solution which is supposed to contain unstable $MnCl_4$. The dark brown solution evolves chlorine gas on warming : $MnO_2+4HCl=MnCl_4+2H_2O$; $MnCl_4=MnCl_2+Cl_2$. Manganese dioxide is unaffected by conc. H_2SO_4 in the cold ; but, on heating below 140°C, manganic sulphate is formed, with the evolution of oxygen. Stronger heating produces manganous sulphate :

$$4MnO_2+6H_2SO_4=2Mn_2(SO_4)_3+6H_2O+O_2 ;$$
$$2Mn_2(SO_4)_3+2H_2O=4MnSO_4+2H_2SO_4+O_2.$$

Concentrated halogen hydracids are oxidised by MnO_2 to the corresponding halogens : $4HX+MnO_2=MnX_2+2H_2O+X_2$ (X=Cl, Br, I). Inspite of its low solubility, manganese dioxide readily reacts with strong reducing agents in the presence of dilute acids. Thus, it reacts with sulphurous acid to form manganous dithionate : $MnO_2+2H_2SO_3=MnS_2O_6+2H_2O$. In the presence of dil. H_2SO_4, manganese dioxide reacts with H_2O_2 to form manganous sulphate and oxygen : $MnO_2+H_2O_2+H_2SO_4=MnSO_4+2H_2O+O_2$. [In absence of acid, MnO_2 also catalytically decomposes H_2O_2 with the evolution of O_2 ; but in this case, half as much oxygen is evolved as in acid solution : $H_2O_2 \xrightarrow{MnO_2} H_2O+\frac{1}{2}O_2$.] As a catalyst, MnO_2 also accelerates the decomposition of $KClO_3$ into KCl and O_2, and the reaction is often used for the preparation of oxygen in the laboratory.

Ferrous sulphate and oxalic acid are quantitatively oxidised by MnO_2 in presence of dil. H_2SO_4 :

$$MnO_2+2FeSO_4+2H_2SO_4=MnSO_4+Fe_2(SO_4)_3+2H_2O ;$$
$$MnO_2+H_2C_2O_4+H_2SO_4=MnSO_4+2CO_2+2H_2O.$$

The molecular constitution of MnO_2 is represented as O=Mn=O.

Evaluation of the purity of pyrolusite : Naturally occuring pyrolusite is the starting material for the production of manganese metal, ferro-manganese and many other useful compounds of the metal. Pyrolusite contains Fe_2O_3 as the chief impurity, along with other minor impurities. For technical purposes, the MnO_2-

content of pyrolusite should be known. The amount of MnO_2 in a sample of pyrolusite is generally estimated by heating a known quantity of the sample with conc. HCl and passing the liberated Cl_2 into a KI solution, and estimating the iodine set free in the process, by a standard solution of sodium thiosulphate, using starch solution as indicator. The estimation may also be carried out by measuring the volume of oxygen at N.T.P., liberated by the reaction of a known weight of the sample with hydrogen peroxide in presence of dil. H_2SO_4.

Uses of MnO_2 : Manganese dioxide is used as a catalyst in the preparation of O_2 from $KClO_3$ in the laboratory and also for the preparation of chlorine. It is also used as an oxidising agent, as a decoloriser for glass, as a depolariser in Leclance cell, as a drier in point, and for glazing pottery.

Manganese tetrachloride ($MnCl_4$) is said to be formed in the deep brown solution obtained by the action of conc. HCl on MnO_2 in the cold. But, the compound cannot be isolated in the solid state. The complex salt, potassium hexachloromanganate, $K_2[MnCl_6]$, can, however, be readily obtained by adding a mixture of solutions of calcium permanganate and potassium chloride to a well-cooled 40% hydrochloric acid solution. It forms very deep red crystals. Ammonium and rubidium salts can be similarly prepared.

Complex fluorides of tetravalent manganese, *viz*. $K_2[MnF_6]$ and $K[MnF_5]$ may be obtained as golden yellow crystals and pale red powder respectively, by the method of preparation similar to that of $K_2[MnCl_6]$.

Manganese disulphate, $[Mn(SO_4)_2]$ is obtained as black crystals on cooling a concentrated solution obtained by oxidising manganous sulphate in sulphuric acid medium with potassium permanganate at 50-60°C. The substance dissolves in conc. H_2SO_4 to form a deep brown solution, but is hydrolysed by water with the deposition of hydrated manganese dioxide. It is a good oxidant.

Compounds of manganese (VI)

The most important compounds of hexavalent manganese are the **manganates** which are the salts of the very unstable *manganic acid* (H_2MnO_4) and are derived from the unknown trioxide, MnO_3.

Potassium manganate (K_2MnO_4) is prepared by fusing manganese dioxide or finely powdered *pyrolusite* with KOH, with free access of air, or mixed with an oxidising agent like KNO_3 or $KClO_3$. The dark green fused mass is cooled and extracted with a small quantity of water when an intense green solution is obtained. The clear solution, on evaporation in vacuum, yields dark green crystals of potassium mangaate, which are isomorphous with corresponding chromates and sulphates.

$$2MnO_2+4KOH+O_2=2K_2MnO_4+2H_2O\ ;$$
$$MnO_2+2KOH+KNO_3=K_2MnO_4+KNO_2+H_2O\ ;$$
$$3MnO_2+6KOH+KClO_3=3K_2MnO_4+KCl+3H_2O.$$

[A very pure sample of K_2MnO_4 may be prepared by adding a mixture of potassium permanganate and potassium hydroxide to water, in complete absence of carbon dioxide : $4KMnO_4+4KOH=4K_2MnO_4+O_2+2H_2O$.]

Sodium manganate (Na_2MnO_4) is similarly prepared from MnO_2 and NaOH ; **Barium manganate** ($BaMnO_4$) is formed as a violet-black precipitate on adding a barium salt solution to a solution of potassium manganate in a little cold water.

Potassium manganate is obtained as dark green crystals of the anhydrous or the hydrated salt, containing different number of molecules of water of crystallisation. It melts at 640-680°C. But, it decomposes into potassium manganite and oxygen when heated near its melting point :

$$2K_2MnO_4=2K_2MnO_3+O_2\uparrow.$$

The salt is highly soluble in alkali solutions, producing green colour. But, it is readily hydrolysed by water, yielding a purple solution of potassium permanganate and depositing hydrated manganese dioxide ; this change occurs more readily on acidification, or on treatment with carbon dioxide. It is actually a disproportionation reaction (or self-oxidation self-reduction reaction), in which a part of Mn (VI) is oxidised to Mn (VII) at the expense of another part which is reduced to Mn (IV) :

$$3Mn\ (VI)=2Mn\ (VII)+Mn\ (IV).$$

The actual reactions are :

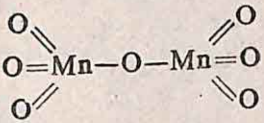
$$3K_2MnO_4+2H_2O=2KMnO_4+MnO_2\downarrow+4KOH\ ;$$
$$3K_2MnO_4+2H_2SO_4=2KMnO_4+MnO_2\downarrow+2K_2SO_4+2H_2O\ ;$$
$$3K_2MnO_4+4CO_2+2H_2O=2KMnO_4+MnO_2\downarrow+4KHCO_3.$$

In a true oxidation reaction, however, a green solution of manganate is completely oxidised to a purple solution of permanganate on passing Cl_2 gas through it, and during the process, no deposition of MnO_2 takes place : $2K_2MnO_4+Cl_2=2KMnO_4+2KCl$.

Potassium manganate is used to prepare green pigments.

Compounds of manganese (VII).

Manganese heptoxide or Permanganic anhydride (Mn_2O_7) is obtained as a heavy green oil (sp.gr.=2·4) by the action of ice-cold conc. H_2SO_4 on pure potassium permanganate: $2KMnO_4 + 2H_2SO_4 = 2KHSO_4 + Mn_2O_7 + H_2O$. The oxide is stable at −5°C and below; but at 0°C, it begins to give off oxygen, although the decomposition is slow upto 10°C. When warmed to 40−50°C, it gives a violet vapour, the decomposition taking place with the evolution of ozonised oxygen and separation of manganous dioxide. It is a very strong oxidising agent, and combustible substances catch fire with its contact. It dissolves in cold water to give a violet solution of permanganic acid ($HMnO_4$), of which it is the anhydride. As the dissolution takes place with the evolution of large amount of heat, partial decomposition of the resultant $HMnO_4$ invariably occurs. The structure of Mn_2O_7 (which is similar to that of Cl_2O_7) is represented as shown below:



Permanganic acid ($HMnO_4$) cannot be obtained as solid. It exists only in dilute solutions (purple-red). It is formed when $MnSO_4$ or $Mn(NO_3)_2$ in hot nitric acid solution is oxidised with lead dioxide, periodic acid or potassium persulphate (in presence of $AgNO_3$ as catalyst):

$$2MnSO_4 + 5PbO_2 + 6HNO_3 = 2HMnO_4 + 2PbSO_4 + 3Pb(NO_3)_2 + 4H_2O\ ;$$

$$2Mn(NO_3)_2 + 5HIO_4 + 3H_2O = 2HMnO_4 + 5HIO_3 + 4HNO_3\ ;$$

$$2MnSO_4 + 5H_2S_2O_8 + 8H_2O = 2HMnO_4 + 12H_2SO_4.$$

The oxidation may also be effected by sodium bismuthate in the cold nitric acid medium:

$$2Mn(NO_3)_2 + 5NaBiO_3 + 16HNO_3 = 2HMnO_4 + 5NaNO_3 + 5Bi(NO_3)_3 + 7H_2O.$$

A pure solution of permanganic acid may be prepared by the reaction of potassium permanganate with hydrofluosilicic acid, or by adding dil. H_2SO_4 to a solution of barium permanganate :

$$2KMnO_4+H_2SiF_6=K_2SiF_6\downarrow+2HMnO_4\,;$$
$$Ba(MnO_4)_2+H_2SO_4=BaSO_4\downarrow+2HMnO_4.$$

The dilute aqueous solution of $HMnO_4$ can be concentrated upto 20% strength ; concentrated solutions decompose to evolve oxygen and deposit manganese dioxide : $4HMnO_4=4MnO_2\downarrow+2H_2O+3O_2\uparrow$. Permanganic acid is a very strong acid.

Permanganates : Among the salts of $HMnO_4$, potassium permanganate is the most important one.

Potassium permanganate ($KMnO_4$) : Potassium permanganate is generally prepared on a large scale. It is prepared by fusing powdered pyrolusite with KOH in free access of air. The resultant green mass of potassium manganate is extracted with water, and CO_2 is passed into the green solution till it reacts slightly acid. The precipitated MnO_2 is filtered and the purple solution is concentrated to obtain crystals of $KMnO_4$. [The reactions involed have been given before.] Potassium permanganate is now-a-days manufactured by electrolytic oxidation of potassium manganate solution, when complete conversion of MnO_4^{2-} to MnO_4^- takes place without separation of MnO_2. In this process, the green K_2MnO_4 solution is electrolysed in a cell with a rotating iron wire-net anode ; the iron inlet pipe of the feed solution acts as the cathode :

$$2MnO_4^{2-}\rightarrow 2MnO_4^-+2e \text{ (at anode) ;}$$
$$2H_2O+2e\rightarrow 2OH^-+H_2\uparrow \text{ (at cathode)}$$
$$\text{or, } 2K_2MnO_4+2H_2O=2KMnO_4+2KOH+H_2\uparrow.$$

The alkaline liquor after electrolysis is filtered through an asbestos bed and the clear purple solution is concentrated to crystallisation.

Properties of $KMnO_4$: Potassium permanganate forms deep purple glistening crystals with a green iridescence. It is moderately soluble in water. It decomposes on heating into potassium manganate, manganese dioxide and oxygen : $2KMnO_4=K_2MnO_4+MnO_2+O_2\uparrow$; at red heat, however, the resultant manganate is further decomposed to give potassium manganite and oxygen : $2K_2MnO_4=2K_2MnO_3+O_2\uparrow$. When heated with H_2SO_4, potassium permanganate decomposes to form $MnSO_4$, with the evolution of oxygen : $4KMnO_4+6H_2SO_4=2K_2SO_4+4MnSO_4+6H_2O+5O_2\uparrow$.

When boiled with concentrated alkali solutions, it is changed into potassium manganate with the liberation of oxygen : $4KMnO_4+$ $+4KOH=4K_2MnO_4+2H_2O+O_2\uparrow$.

Potassium permanganate is a strong oxidising agent. When mixed with powdered sulphur or charcoal, it burns violently. A mixture of powder $KMnO_4$ and powdered oxalic acid spontaneously inflames within a few seconds. It oxidises conc. hydrochloric acid into chlorine in the cold : $2KMnO_4+16HCl=2KCl+2MnCl_2+8H_2O$ $+5Cl_2$. The oxidising action of $KMnO_4$ differs according as the reaction is carried out in acidic, neutral or alkaline medium. [See Vol. I, p. 256.] The oxidation by $KMnO_4$ in acidic (H_2SO_4) solution is illustrated by the following reactions, many of which are used in volumetic analysis :

Ferrous salts are oxidised to ferric salts :

$$2KMnO_4+10FeSO_4+8H_2SO_4=K_2SO_4+2MnSO_4+5Fe_2(SO_4)_3+8H_2O.$$

Iodine is liberated from KI solution :

$$2KMnO_4+10KI+8H_2SO_4=6K_2SO_4+2MnSO_4+5I_2+8H_2O.$$

Oxygen is liberated from H_2O_2 :

$$2KMnO_4+3H_2SO_4+5H_2O_2=K_2SO_4+2MnSO_4+5O_2+8H_2O.$$

Oxalic acid is oxidised to CO_2 :

$$2KMnO_4+5H_2C_2O_4+3H_2SO_4=K_2SO_4+2MnSO_4+10CO_2+8H_2O.$$

Sulphur dioxide is oxidised to H_2SO_4 :

$$2KMnO_4+5SO_2+2H_2O=K_2SO_4+2MnSO_4+2H_2SO_4.$$

Nitrites are oxidised to nitrates :

$$2KMnO_4+5KNO_2+3H_2SO_4=K_2SO_4+2MnSO_4+5KNO_3+3H_2O.$$

In neutral solutions, potassium permanganate oxidises hot solution of a manganous salt (in presence of ZnO) to MnO_2. This reaction serves as the basis of *Volhard's method* of estimation of manganese (ZnO removes the acid produced) :

$$2KMnO_4+3MnSO_4+2H_2O=5MnO_2+K_2SO_4+2H_2SO_4.$$

Under similar condition, potassium permanganate decomposes H_2O_2 with the formation of MnO_2, and oxidises sodium thiosulphate to sodium sulphate : $2KMnO_4+3H_2O_2=2KOH+2MnO_2+2H_2O+$ $3O_2$; $8KMnO_4+3Na_2S_2O_3+H_2O=8MnO_2+3Na_2SO_4+3K_2SO_4$ $+2KOH$

In alkaline medium, $KMnO_4$ solution oxidises KI to KIO_3:
$2KMnO_4+H_2O+KI=2MnO_2+2KOH+KIO_3$.

Uses: Potassium permanganate is used as an oxidant in preparative and analytical chemistry. It is also used in gargles and mouth-washes as an antiseptic, as a bleaching agent and for preparing pure distilled water.

Sodium permanganate ($NaMnO_4$) is prepared in a manner similar to that of $KMnO_4$, but the solution cannot be easily crystallised. The solution of $NaMnO_4$ is generally used as a disinfectant (*Condy's fluid*).

Analytical applications of potassium permanganate: As already stated, potassium permanganate is a strong oxidant and many of its oxidation reactions have been successfully utilised for accurate volumetric analysis. The advantage of the reagent lies in the fact that its solution is intensely coloured and as it is used as the titre, no external indicator is necessary to determine the end-point; the appearance of the pink colour of the solution indicates the completion of the titration. The draw-back of the reagent is the bad keeping quality of its solution, whose strength gradually deteriorates due to slow decomposition into MnO_2. [This is actually an autocatalytic process, aggravated by MnO_2 formed by the reduction of MnO_4^- by organic matter of distilled water, or the traces of the dioxide present in $KMnO_4$ itself.]. For this reason, the reagent solution is to be standardised (against sodium oxalate or Mohr's salt) before accurate determinations. Further, as $KMnO_4$ is not generally available in perfectly pure condition, it cannot be used as a *primary standard*. The solution of $KMnO_4$ should be stored in dark coloured bottles as it is photochemically decomposed by direct light.

Potassium permanganate quantitatively reacts with reducing species in the acidic medium according to the equation: $MnO_4^- + 8H^+ + 5e = Mn^{++} + 4H_2O$. Hence, the equivalent weight of $KMnO_4$ in such reactions is $\frac{1}{5}$ of its molecular weight. So, 1 ml. of a 0·1N $KMnO_4$ soln. is equivalent to $\frac{1}{10}$ milliequivalent of the reducing species in such reactions. Fe(II), oxalates, formates, H_2O_2, nitrites *etc.* are generally estimated by $KMnO_4$ in acidic media. In alkaline or neutral medium, $KMnO_4$ oxidises manganous salts to MnO_2 and is itself reduced to MnO_2; the half-equation of this reaction is, $MnO_4^- + 4H^+ + + 3e = MnO_2 + 2H_2O$. In this case, the equivalent weight of $KMnO_4$ is $\frac{1}{5}$ of its molecular weight (see Vol. I, p. 257). Calcium can be estimated by precipitating the metal as calcium oxalate, thoroughly washing the precipitate and then titrating it with $KMnO_4$ soln. in warm dil. H_2SO_4 medium. Oxidising agents can also be estimated in an indirect way by $KMnO_4$, by first treating them with a known excess of a reducing agent and then back-titrating the residual reducing agent.

Complexes of manganese : Manganese forms a large varieties of complexes in its different oxidation states. In fact, many oxidation states of the metal, which are quite unstable to form simple compounds, can be more or less stabilised by complex formation. We shall confine our discussion here to the complexes of Mn(II), Mn(III and Mn(IV).

Mn(II) complexes : Among the octahedral complexes, the hexoaquo cation, $[Mn(H_2O)_6]^{++}$ is not very stable, but the hexammine $[Mn(NH_3)_6]^{++}$ is more stable. Other octahedral species include complexes with ethylene diamine, oxalate, EDTA *etc.* A number of tetrahedral complexes of Mn(II) are known, of which the tetrahalo anions $[MnX_4]^{2-}$ are important.

Mn(III) complexes : In the trivalent state, manganese forms more or less stable halo-complexes like $[MnCl_5]^{2-}$, $[MnCl_4]^{-}$, $[MnF_5]^{2-}$, $[MnF_4]^{-}$ *etc.* The tris-acetylacetonato, tris-oxalato and tris-malonalo-complexes of Mn(III) are also well-characterised. Salts of complex $[Mn(CN)_6]^{3-}$ ion are also known.

Mn(IV) complexes : The chloro- and fluoro-complexes of Mn(IV) have already been discussed. Complex ions of the type $[Mn(IO_3)_6]^{2-}$ are also known.

Tests of Manganese : (i) A manganese compound, on fusion with Na_2CO_3 and KNO_3, form a green mass of manganate. (ii) A manganese compound, on oxidation with PbO_2 or sodium bismuthate in nitric acid medium, produces a pink colour of $HMnO_4$. (iii) A solution of manganous salt produces a flesh-coloured precipitate of MnS on passing H_2S in ammoniacal solution. (iv) Manganese salts stains the microcosmic salt bead violet in the oxidising flame.

Manganese is gravimetrically estimated by precipitating as $MnNH_4PO_4.H_2O$, and weighing as $Mn_2P_2O_7$ by igniting the washed precipitate. Volumetrically, manganese is estimated by oxidising it to $HMnO_4$ with sodium bismuthate, adding known excess of Mohr's salt to the filtered soln., and then back-titrating with standard $KMnO_4$ soln. It can also be estimated by Volhard's method (See vol. I, p. 255).

CHAPTER XX

IRON, COBALT AND NICKEL. THE METALS OF THE EIGHTH GROUP

The eighth group of the periodic table contains nine metals which constitute three series of three consecutive elements each. In these three sets or *triads* of metals, the elements are placed side by side in the order of their increasing atomic numbers. The first triad comprises iron, cobalt and nickel (atomic numbers 26, 27 and 28 respectively), having very close resemblance to one another, and is generally known as the **iron group.** The other two triads contain elements with atomic numbers 44 to 46 (ruthenium, rhodium and palladium) and 76 to 78 (osmium, iridium and platinum), and these are collectively known as the **platinum metals.** Each of these triads actually represents the central part of the series of transitional elements occuring in each of the three long periods of the periodic table. Thus, the metals of the iron group occur practically in the middle of the elements of the *first transitional series*, starting from scandium and ending in zinc. We shall restrict our discussion in this chapter among the members of the iron group, *i.e.* among the metals iron, cobalt and nickel. Some important physical properties of the three metals are stated in the table below : (*See Table 20·1*). [It may be noted that we shall be dealing in the following section the comparative chemistries of the elements placed in a horizontal series, and not in a vertical series as was done with the other elements in the previous chapters.]

The horizontal similarities between the metals of the iron group are greater than anywhere else in the periodic table, except among the lanthanides.

Occurrence : In all probability, iron is the most abundant metal available in earth's crust. The core of the earth appears to consist largely of iron, together with considerable amount of nickel. The abundance of these three metals in earth's crust is as follows : Iron, 5% ; Cobalt, $2{\cdot}3 \times 10^{-3}$ % ; Nickel, 8×10^{-3} %. None of these metals

TABLE 20·1

Property	Iron	Cobalt	Nickel
Atomic weight	55·84	59·97	58·68
Atomic number	26	27	28
Electronic configuration	[Ar] $3d^6 4s^2$	[Ar] $3d^7 4s^2$	[Ar] $3d^8 4s^2$
Density (gm/c.c.)	7·85	8·8	8·9
Atomic volume (c.c.)	7·1	6·7	6·6
Melting point (°C)	1533	1480	1455
Boiling point (°C)	2880	2900	2840
Electrode potential (v) M/M^{++} (25°C)	−0·44	−0·28	−0·23

occurs free in nature (except in small quantities in some meteorites). They occur together, not only in the periodic table, but also in nature as the sulphide, arsenide and silicate minerals. (Iron, however, occur extensively as the oxide ores,)

Gradation of some physical properties : As already stated, iron, cobalt and nickel are placed side by side along a horizontal series with serial atomic numbers 26, 27 and 28 respectively. As a result, much conspicuous differences among their properties are not expected. Thus, their **atomic weights** differ by small amounts. All of them are **typically metallic** in appearance and behaviour and all these metals are hard, malleable and ductile. Their **density** increases slightly from iron to cobalt, which is practically as dense as nickel. Their high **melting points** show gradual but small decrease from iron to nickel, but the **boiling points** are anomalous. The **atomic radii** (and consequently the **atomic volumes**) are small and they show very small decrease from Fe to Co, but are almost the same for Co and Ni. All these metals are **magnetic substances**—the magnetism of iron being the greatest. They are **catalytically active** ; finely divided nickel is most active in this respect and cobalt is intermediate between nickel and iron with regard to this activity. In the finely divided state, all these three metals occlude hydrogen.

Chemical properties : In their chemical properties, the three metals of this *triad* show close resemblances which are reflected in the following :

(*a*) *Electropositive character* : The three metals are placed just below zinc in the electromotive series, and as such, they behave as fairly electropositive elements. The electropositive character of these metals, however, gradually decreases with the increase of atomic number. *This trend is observed in practically all the chemical properties of these three metals.* All the three metals liberate hydrogen from dilute acids, but the reactivity decreases in the order Fe→Co→Ni.

(*b*) *Reaction with steam* : Red-hot iron decomposes steam with the production of Fe_3O_4, but under similar condition, Co and Ni decompose steam with the formation of CoO and NiO.

(*c*) *Action of conc.* HNO_3 : All the three metals are rendered passive by conc. HNO_3.

(*d*) *Action of moist air* : Iron, on exposure to moist air, rusts with the formation of hydrated oxide ; but cobalt and nickel are not affected by moist air.

(*e*) *Preparation of the metals* : All the three metals are prepared by the reduction of their oxides by carbon or carbon monoxide.

(*f*) *Oxidation states* : As already stated, Fe, Co, and Ni belong to the first transition series of the periodic table and as such, they exhibit variable valency. The principal oxidation states of these metals are :

$$Fe(+2, +3, +6) ;\ Co(\mathbf{+2}, +3, +4) ;\ Ni(\mathbf{+2}, +3\ +4)$$

[The most stable oxidation states are written in bold letters.] A remarkable feature of this triad is the decrease in the stability of the +3 oxidation state of the members (in their simple salts) with the increase in atomic number. In iron compounds, the Fe^{+3} salts are more stable than the Fe^{+2} salts, while the Co^{+2} and Ni^{+2} salts are more stable than their simple salts in the trivalent state. Simple Ni (III) salts are not known ; but Ni (IV) compounds like K_2NiF_6 and $BaNiO_3$ are known. Trivalent cobalt is very common among the complex compounds and this is due to the large decrease in the E^0 value of the $Co^{+3}+e\rightarrow Co^{+2}$ system (which is 1·82 volts at 20°C) owing to the preferential complexation of the +3 oxidation state. Hexavalent iron is known in ferrates which are strong oxidising agents (even stronger them permanganate). Tetravalent cobalt and nickel occur in complex salts and also in oxides. Due to their variable valency, the salts of these metals often take part in red-ox reactions. Because of the presence of one or more unpaired electrons in most of their oxidation states, these metals form salts of different colours in their different oxidation states. These colours are generally : Fe^{+2} (pale green), Fe^{+3} (yellow) ; Co^{+2} (pink), Co^{+3} (blue or yellow) ; Ni^{+2} (blue or bluish green).

(*g*) *Nature of compounds* : (i) **Oxides** : All these metals are oxidised on heating in air to give the oxides. The oxide of the type MO, in which the metals (M) exhibit bivalency, are formed by all the three metals and they are basic in character. The oxides M_2O_3 of the metals in their +3 oxidation state are much less basic than the oxides of the type MO, and in fact they are amphoteric to some extent. [But, although Fe_2O_3 gives rise to stable *ferrites* like $Na_2Fe_2O_4$ on fusion with sodium carbonate, Co_2O_3 and Ni_2O_3 do not form such compounds.] Mixed oxides like Fe_3O_4 and Co_3O_4, containing the metals in +2 and +3 oxidation states, are also formed. Cobalt and nickel form oxides of the type MO_2 in which the metals exhibits tetravalency. The oxides are capable of forming *cobaltites* and *nickelites*. Iron does not form oxide in the tetravalent state, but it forms *ferrates* ; corresponding to the unknown acidic oxide FeO_3.

(ii) **Hydroxide :** Fe, Co and Ni form hydroxides in the bivalent state. Of these, $Fe(OH)_2$ $Co(OH)_2$ are easily oxidised in air, but $Ni(OH)_2$ is quite stable. Hydroxides of these metales in their trivalent states are also known.

(iii) **Chlorides :** Iron forms chlorides both in the bivalent and the tervalent states *e.g.* $FeCl_2$ and $FeCl_3$, of which the latter is more stable. The other-two metals give chlorides in the bivalent state only, such as $CoCl_2$ and $NiCl_2$. The hydrated crystals of ferrous and ferric chlorides correspond to the composition $FeCl_2.4H_2O$ and $FeCl_3.6H_2O$ respectively, but those of cobalt chloride and nickel chloride have the composition $CoCl_2.6H_2O$ and $NiCl_2.6H_2O$ respectively. All these chlorides are strongly hygroscopic. The other halides are similar in nature and property.

(iv) **Sulphates :** In the bivalent state, all the three metals forms sulphates whose hydrated forms, $MSO_4.7H_2O$, are isomorphous due to the nearly equal ionic radii of the metal ions, M^{+2}. These sulphates have a remarkable tendency to form double sulphates of the type $MSO_4.M^I_2SO_4.6H_2O$ (where $M=Fe^{+2}$, Co^{+2}, Ni^{+2} and $M^I=NH_4^+$) which are isomorphous with one another. Iron and cobalt form sulphates in trivalent state also. Alums cotaining ferric iron and cobaltic cobalt are isomorphous.

(v) **Sulphides :** All the three metals form sulphides in the bivalent state, and these are precipitated as black substances on passing H_2S in ammoniacal medium. Of these sulphides, FeS is soluble in dilute mineral acids, whereas CoS and NiS are soluble in conc. HCl, HNO_3 or in aqua regia. Ferric sulphide (Fe_2S_3) and iron disulphide (FeS_2) are also known, but the corresponding compounds are not formed by cobalt and nickel.

(vi) **Nitrates :** Fe, Co and Ni form water-soluble crystalline nitrates of analogous compostion, $M(NO_3)_2.\ 6H_2O$, in their bivalent states. Ferric nitrate is also known, but Co(III) and Ni(III) nitrates are unknown. All the nitrates are very hygroscopic in nature.

(vii) **Carbonyls :** Iron, cobalt and nickel resemble one another in forming covalent carbonyls with carbon monoxide (See p. 21 of this volume). Common among them are $Fe(CO)_5$, $Co_2(CO)_8$ and $Ni(CO)_4$, of which $Fe(CO)_5$ and $Ni(CO)_4$ are volatile, while $Co_2(CO)_8$ is a solid.

(viii) **Complex compounds :** All these three metals form wide varieties of complex compounds. The capability of complex-formation of these metals is due to their low ionic radii and comparatively large ionic charge and availability of vacant orbitals of appropriate energy, which are utilised for bonding purposes. In this capcaity, cobalt has been found to be intermediate between iron and nickel. They form both complex cations and anions. In the complex cyanides, iron forms both ferrocyanides, $[Fe(CN)_6]^{4-}$, and ferricyanides, $[Fe(CN)_6]^{3-}$, of which the ferrocyanides are more stable ; $K_3[Fe(CN)_6]$ decomposes on exposure to light into $K_4[Fe(CN)_6)]$. Cobalt also forms cobatocyanides and cobalticyanides, similar in composition to the iron compounds ; but in this case, the cobalticyanides are more stable than the cobaltocyanides which readily changes into the former by aerial oxidation. Nickel forms two types of cyanide complexes like $K_2[Ni(CN)_4]$ and $K_3[Ni(CN)_4]$, in which it exhibits bivalency and monovalency respectively ; but, these also are not so stable as the ferrocyanides or the cobalticyanides, and are dissociated in solution to certain extent to yield free Ni^{++} ions. [In all these cases, the metals form the complex anions.] Among these metals, cobalt [used in the form of $CoCl_2$ or other Co(II) salts] is conspicuous in forming stable complexes in ammoniacal medium, and these are known as *cobaltammines*. In these complexes, the metal forms complex cations, *e.g.* $[Co(NH_3)_6]^{+3}$, $[Co(NH_3)_5Cl]^{+2}$, $[Co(NH_3)_4Cl_2]^{+1}$ *etc.*

COMPARISON AMONG IRON, MANGANESE AND CHROMIUM.

Chromium, manganese and iron occur in the fourth period of the Periodic Table, belonging to Grs. VIA, VIIA and VIII respectively. But, there are many close resemblances between these three metals. All of them are transitional metals which are very hard with high melting and boiling points. All of them exhibit variable valencies and form coloured and paramagnetic compounds. All these metals or their oxides are used as catalyst (generally in the finely divided state) in many syntheses. But, while chromium and manganese are diamagnetic, iron is paramagnetic.

Chemical properties of chromium, manganese and iron are also analogous in many respects. All of them react with steam to produce hydrogen : $2Cr+3H_2O=Cr_2O_3+3H_2\uparrow$; $Mn+2H_2O=Mn(OH)_2+H_2\uparrow$; $3Fe+4H_2O=Fe_3O_4+4H_2\uparrow$. Hydrogen is also liberated by the reactions of the three metals with dilute acids : $Cr+2HCl=CrCl_2+H_2\uparrow$; $Mn+2HCl=MnCl_2+H_2\uparrow$; $Fe+2HCl=FeCl_2+H_2\uparrow$. The reactivity in these reactions decreases in the reverse order of the atomic numbers of the metals, which is reflected in their relative positions in the electrochemical series. Both Cr and Fe are rendered *passive* by conc. HNO_3, but Mn alone react with dilute HNO_3 to liberate hydrogen : $Mn+2HNO_3=Mn(NO_3)_2+H_2\uparrow$.

At elevated temperatures, only Mn and Fe react with carbon, sulphur and chlorine to form binary compounds. Only Mn combines with nitrogen at high temperatures to form a nitride.

All the three metals form oxides in the bivalent state, *viz.* CrO, MnO and FeO, which are basic in character. The stabilities of these oxides follow the order : $CrO < FeO < MnO$. Similar trend in the stabilities is also observed in the simple salts of the metals in their bivalent states. The analogy between MnO and FeO is manifested in the fact that, both of them dissolve in acids to produce manganous and ferrous salts respectively, which are capable of combining with certain alkali metal salts to give rise to isomorphous double compounds. Manganous salts, however, surpass the ferrous salts in stability. In the trivalent state, the metals form oxides of the type R_2O_3 which are quite stable and mainly basic. The simple salts derived from these oxides are quite stable in the cases of Cr and Fe, but the tervalent manganese salts are generally unstable (except manganic fluoride, acetate and some phosphates, which are more or less stable). The similarity between Mn_2O_3 and Fe_2O_3 is also exhibited by the formation of isomorphous alums, *viz.* manganic alum, $(NH_4)_2SO_4 . Mn_2(SO_4)_3 . 24H_2O$ and ferric alum, $(NH_4)_2SO_4 . Fe_2(SO_4)_3 . 24H_2O$. The simple salts of the tervalent metals, however, usually hydrolyse in aqueous solutions. Manganese and iron also form the mixed oxides of the type R_3O_4, which is absent in the case of chromium. In the tetravalent state, both Mn and Cr form oxides of the type RO_2 ; but Fe does not form such an oxide. Oxide of hexavalent chromium, CrO_3, is known ; it is highly acidic. MnO_3 and FeO_3 are not known in the free state. But, the corresponding manganates and ferrates (such as K_2MnO_4 and K_2FeO_4) are known, which are isomorphous with K_2CrO_4.

All the three metals form similar complex cyanides both in the bivalent and tervalent states, such as chromocyanides and chromicyanides, manganocyanides and manganicyanides, ferrocyanides and ferricyanides.

IRON

Occurrence : Iron occurs abundantly in nature, second perhaps only to aluminium. It constitutes about 4·2% of the earth's crust. As it is a fairly electropositive metal, it seldom occurs native, but is widely available in combination with other elements, mainly as oxides, sulphide and carbonate. The important ores of iron are : the oxide ores, *viz.* **haematite (Fe_2O_3)**, **magnetite (Fe_3O_4)**, **limonite ($2Fe_2O_3.3H_2O$)** ; the carbonate ore, *viz.* **siderite** or **spathic iron ore ($FeCO_3$)** ; the sulphide ores, *viz.* **iron pyrites (FeS_2)** and **copper pyrites ($CuFeS_2$)**.

Concentrated iron ores are available in large quantities in many parts of the world. In India, rich deposits of haematite are available in Orissa, Bihar, West Bengal, Tamilnadu, Karnatak, Madhya Pradesh and Andhra Pradesh. Iron is extracted in this country mainly from haematite. Magnetite and siderite are also utilised at certain places for the extraction of iron, but the sulphide ores are seldom used for this purpose.

Pure iron is rarely used for any important purpose, and in fact, it is also very difficult to obtain chemically pure iron on a large scale, especially to free it from carbon. All commercial iron are actually alloys of iron with various proportions of carbon, along with small quantities of some other metals and non-metals. Depending mainly upon its carbon-content, commercial iron is generally divided into three categories, *viz.* (i) **Cast** or **pig iron**, (ii) **Steel** and (iii) **Wrought iron**. Cast iron generally contains 2·0 – 4·5% carbon ; steel about 0·15 – 1·5% carbon and wrought iron about 0·1 – 0·25% carbon. Iron is first obtained as cast iron during its metallurgy ; steel and wrought iron are usually prepared from cast iron.

Extraction of iron : The extraction of iron from haematite consists of two operations, *viz.*, (i) **Calcination** or **roasting**, which is followed by (ii) **Smelting** or the reduction of the roasted ore. [When low-grade oxide ores are used, preliminary washing and magnetic separation is sometimes necessary.]

(1) **Calcination or Roasting :** This operation is carried out by burning the ore with a little coal in shallow kilns with large access of air. Moisture, CO_2 (from carbonates), some sulphur and arsenic are driven off in the process and all the iron is converted into ferric oxide. The ore also becomes porous in the process and this helps better reduction during smelting. The powdered ore (roasted) is agglomerated by sintering, or briquetted into lumps of suitable size by the addition of some binding agent.

(2) **Smelting :** This operation is carried out in a blast furnace and it takes place in three stages, *viz*. (i) the reduction of ferric oxide to metallic iron by CO and C, (ii) removal of siliceous gangue materials of the ore as calcium silicate (slag) by fluxing with the added limestone and (iii) melting of the iron and the slag by high temperature of burning coke and hot air blast. The two separate molten layers of the metal and the slag are then taken out separately through two different outlets situated near the bottom of the blast furnace.

The sintered roasted ore and about one-fourth of its weight of limestone are mixed together outside the furnace. It is then poured inside the blast furnace, through a cup-and-cone arrangement at its top, in alternate layers of half its weight of metallurgical coke, which serves both as reducing agent and fuel.

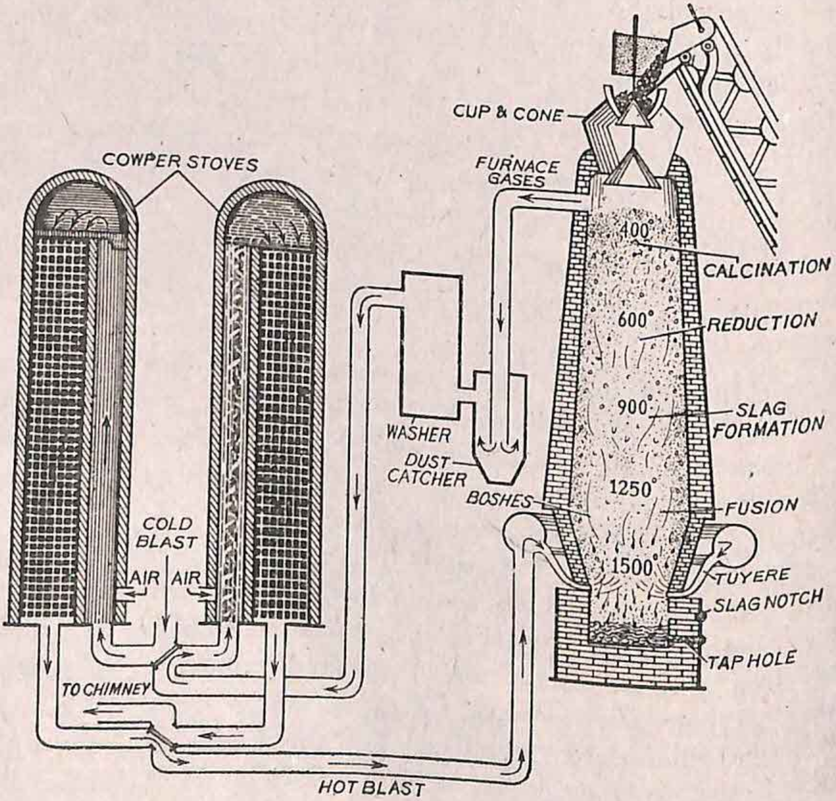


Fig. 20.1—Blast furnace with Cowper stoves.

The working of the blast furnance is started by burning wood on the hearth of the furnace. The hot gases coming out through the flue of the furnace are passed through dust catcher and washer, mixed with dry and clean air and burnt alternately in two *Cowper stoves* to about 800°C. The dry and hot air is then blown into the furnace, just above its hearth, through a number of water-jacketted iron pipes called *tuyers*, by means of powerful blowers.

Function of the Cowper stoves : The Cowper stoves, used with the blast furnace during the extraction iron, function as heat-regenerators. The **blast furnace gases,** leaving the furnace during the extraction of iron, contain by volume about 12% CO_2, 28% CO, 4% CH_4 and 56% N_2. The large amount of CO, present in the gas-mixture, is burnt in the Cowper stoves to generate heat to preheat the incoming air-blast. This economises fuel and helps to maintain the required high temperature inside the blast furnace.

The hot furnace-gases escape through an outlet near the top of the furnace and are then led to the Cowper stoves through a *dust catcher* and *washer.* The stoves are cylindrical iron towers which are lined inside with firebricks and packed with chequer brick-work, having a chanel at one side, where the furnace-gases are burnt. The hot products of combustion heat up the brick-work of the stoves. The two stoves are used alternately. When one stove is heated by the combustion of the furnace-gases to a high temperature, the coming gases are led to the other stove and are burnt there. Meanwhile, dry air is pumped by blowers through the heated stove and the preheated air-blast is sent into the furnace through the tuyeres. By the time this stove is cooled, the other one becomes sufficiently heated to preheat the air-blast to the required temperature, and so the air is allowed to pass through it and the furnace-gases are again led to the cooler stove for combustion. Thus, a continuous hot air-blasts through the tuyeres are maintained by regenerating heat from the combustion of the furnace-gases.

Reactions occuring in the blast furnace during the extraction of iron : A large number of consecutive and simultaneous reactions of complicated nature take place at different zones of the blast furnace during the metallurgy of iron. For the convenience of depicting these reactions, the entire length of the blast furnace may be divided into three zones of different temperature ranges, and the nature of chemical changes that occur at any particular zone may be easily discussed.

The temperature inside the blast furnace is about 400°C near its mouth and it increases gradually downwards, reaching a maximum of about 1500°C near the hearth. The hot coke in the hearth of the furnace burns to carbon monoxide by the hot and dry air-blast through the tuyeres. [With excess of hot air available at the mouth of the tuyeres, carbon is oxidised first to CO_2, which is subsequently reduced to CO on passing through the upper layer of white-hot coke : $C+O_2=CO_2$; $CO_2+C=2CO$.]

At the upper part or the *throat* of the furnace (near its mouth), the charge inside is preheated and dried at a temperature of about 400°C prevailing there. In the process of descending through the furnace, the charge arrives at zones of gradually higher temperatures (see fig. 20.1). At the region where the temperature exceeds 400°C, Fe_2O_3 is reduced by the ascending CO into Fe_3O_4 and partly to FeO :

$$3Fe_2O_3+CO \rightleftharpoons 2Fe_3O_4+CO_2 ;$$
$$Fe_2O_3+CO \rightleftharpoons 2FeO+CO_2.$$

At somewhat lower region, Fe_3O_4 is also reduced to FeO at a temperature little above 500°C : $Fe_3O_4+CO \rightleftharpoons 3FeO+CO_2$. A little further down the furnace, the prevailing temperature is above 600°C, and FeO is reduced here to metallic iron : $FeO+CO \rightleftharpoons Fe+CO_2$. During this process, the resultant CO_2 is reduced by the hot carbon to CO, but a portion of CO is simultaneously decomposed in contact with spongy iron into CO_2 and carbon. Thus, the following equilibrium is established : $2CO \rightleftharpoons CO_2+C$. At a region where the temperature is about 900°C, the glowing particles of carbon (resulting from the above equilibriated reaction) and the carbon of the coke itself complete the reduction of the oxides of iron into metallic iron : $Fe_3O_4+C \rightleftharpoons 3FeO+CO$; $FeO+C \rightleftharpoons Fe+CO$. Decomposition of limestone (used as flux with the ore) into CaO and CO_2 takes place at this stage, and the resulting CaO combines with the siliceous impurities of the ore to form a slag of mainly calcium silicate : $CaCO_3 \rightleftharpoons CaO+CO_2$; $CaO+SiO_2=CaSiO_3$. The spongy iron absorbs at this region a considerable amount of carbon to form iron carbide, Fe_3C (cementite) and also some sulphur from the fuel used. Some phosphorus is also formed here through the reduction of phosphate in the ore and is absorbed by iron : $Ca_3(PO_4)_2+3SiO_2=3CaSiO_3+P_2O_5$: $P_2O_5+5Fe+5SiO_2=5FeSiO_3+2P$. At a little higher temperature, some silicate is reduced to silicon and is alloyed with iron : $SiO_2+2C=Si+2CO$. Calcium sulphate, present as an impurity in the ore is reduced here by iron and carbon to ferrous sulphide : $CaSO_4+Fe+3C=CaO+FeS+3CO$. Oxides of manganese, present in iron ore, are also reduced here to the metallic state and is alloyed with iron.

Near the bosches of the furnace, the temperature is about 1100°C. The impure spongy iron (containing C, S, Si, P and Mn as impurities) melts here along with the slag. The fused mixture travels down to the hearth of the furnace (temperature about 1500°C) and settles there in two distinct layers—the molten metal below and the lighter fused slag above it. The layer of slag protects the molten iron from the oxidising action of the hot air-blast through the tuyeres.

The slag is removed at intervals through the slag-notch, while the molten metal is taken out through the tap-hole and cast into sand moulds to obtain cast iron, or is directly transferred to the steel-making furnace in the fluid state. The whole process is continuous and the furnace is allowed to run for years, until it is put out of commission for repair.

Cast iron or pig iron is a hard, brittle and crystalline solid, and as such, it is not used for structural purposes. It is the most impure form of commercial iron with variable composition. A representative sample may contain 2–5% C, 1–2% Si, 0·5–1% P, 0·3–1% S and 0·2–1% Mn, the rest being iron. [In cast iron, carbon is present both in the free graphitic state or as carbide, Fe_3C (cementite), sulphur as sulphide (FeS), phosphorus as phosphide (Fe_3P), silicon as silicide (FeSi) and manganese as the free metal. Cast iron melts at about 1200°C and expands on solidification. It is, therefore, used as a good casting metal for the fabrication of drain pipes, gutters, covers of man-holes, railings etc.

Cast iron (or pig iron) is usually distinguished into two varieties, *viz*. **grey cast iron** and **white cast iron.** In the grey variety, carbon is present mainly as graphite, while in the white variety, it exists in the combined state as *cementite*, Fe_3C. The former dissolves in HCl with the evolution of H_2 and separation of a black residue of graphite ; but, the latter gives a mixture of H_2 and hydrocarbons on such treatment. The approximate composition (per cent) of the two varieties are given below :

		White	*Grey*
Graphitic carbon	...	3·045	—
Combined carbon	...	0·704	2·98
Silicon	...	2·003	0·96
Manganese	...	0·309	0·505
Phosphorus	...	0·037	1·41
Sulphur	...	0·008	0·28
Iron	...	Rest	Rest

Blast furnace slag contains mainly calcium silicate, together with some aluminium silicate. It is used for making cement and paving stone and also for metalling roads and for reclaiming low and waste lands. It also acts as a manure.

Manufacture of wrought iron or Malleable iron : Wrought iron is purer than any other form of commerical iron (*viz*. cast irom and steel). It is manufactured from cast iron by removing most of the impurities by a process known as the *puddling process*. Wrought iron is about 99·5% pure iron, containing 0·1 – 0·25% carbon, the rest being sulphur, silicon, phosphorus and manganese.

In the *puddling process*, blocks of cast iron is smelted in a reverberatory furnace with a lining and bed of Fe_2O_3 or haematite. Silicon, manganese and phosphorus in the cast iron are oxidised to their oxides by Fe_2O_3 and then combine with it to form slag ; sulphur is oxidised to SO_2 and is thus eliminated ; carbon is partly burnt to CO and escapes. The molten mass on the hearth of the furnace is frequently stirred or '*puddled*' with a long iron pole (hence the name of the process), so that it comes into intimate contact with the furnace lining or the bed to bring about effective oxidation of the impurities. The slag is removed from the upper surface of the molten mass. The melting point of cast iron gradually increases with the elimination of impurities present in it, and so it becomes pasty. The pasty material is collected in big lumps or *blooms* (each about 40 kg. in weight) and squeezed under a steam hammer to remove most of the contaminated slag. The wrought iron, thus produced, is forged into bars.

Wrought iron melts at 1530°C. It is malleable but tough, and possesses a high tensile strength. It can be forged and welded. Wrought iron does not harden on heating to redness and subsequent quenching in cold water. It is generally used for making nails, bolts, chain, sheets, anchor, agricultural equipments, pipes, rails, rods, beams, magnets and utensils.

Manufacture of Steel : So far as the carbon-content is concerned, steel is intermediate between cast iron and wrought iron. The percentages of silicon, phosphorus and sulphur are also less in steel than in cast iron, but the manganese-content is often higher. Some other metals like chromium, vanadium, tungsten, nickel, cobalt, molybdenum and sometimes manganese are also incorporated during the manufacture of steel for the development of some desired and useful properties in it. The requisite carbon-content in steel can, therefore, be attained either by removing some carbon (along with S, P and Si) from cast iron and then adding the required amounts of the other elements, or by increasing the carbon-content of wrought iron by adding carbon (along with some other required elements) from outside. In yet another process, steel can be manufactured directly from pure iron ore and carbon in an electric furnace. Depending upon the nature of the reactions involved in the steel-making, the following processes have been developed :

(1) **The Cementation process.** } From pure wrought iron.
(2) **The Crucible process.**
(3) **The Open-hearth or Siemens-Martin process.** } From cast iron.
(4) **The Bessemer process.**
(5) **The Electric furnace process.**—From pure ore and carbon.

Now-a-days, however, the major portion of the steel is manufactured by the open-hearth and the Bessemer processes from cast iron. According to the amount of phosphorus present in cast iron, each of the above two processes is modified into two different ways. If the cast iron is free from or poor in phosphorus, *the acid process* is used, while for the cast iron with high phosphorus-content, *the basic process* is employed.

1. **The Cementation process :** Carburization (*i.e.* the incorporation of carbon) of wrought iron is effected in this process by packing its bars in charcoal powder in fireclay boxes and heating at red heat. Carbon is thus gradually absorbed by wrought iron in the solid state and steel is thereby formed. The duration of heating (which may extend upto several weeks) is adjusted according to the

amount of carbon intended to be incorporated in the wrought iron. The steel produced in the process has blistered appearance at the surface and in commonly known as '*blister steel*'. This is melted in big plumbago crucibles and cast into moulds (*cast steel* or *crucible steel*).

[It has been suggested that, during the cementation process, solid carbon is not directly absorbed by the wrought iron to produce steel, as such an affair is possible only under very high pressure. Hot charcoal is possibly oxidised first to CO by the action of the limited amount of air enclosed in the boxes and this serves as the carburizing agent. Such carburization is also caused by gaseous hydrocarbons, cyanogen *etc.*]

Case-hardening : Wrought or mild iron is often given a superficial coating of steel by heating it in contact with powdered carbon or potassium ferrocyanide. Case-hardened steel is very hard at the surface, but flexible and soft inside. Armour plates are generally prepared by this process. The cementation process, as described above, is mainly used now-a-days to prepare case-hardened steel.

Nitriding : This is another process to prepare surface-hardened steel. Here the steel objects are heated at 500-600°C for 60-80 hours in partially dissociated (33%) ammonia ($2NH_3 \rightleftharpoons 2N + 3H_2$), when the atomic nitrogen is absorbed by steel at the surface to form a very hard coating of metal nitrides.

2. **The Crucible process :** In this process, wrought iron is melted in fireclay crucibles with the required amount of charcoal powder, when steel is formed. This is a very costly process and is used to prepare certain high class steel for the fabrication of razor-blades, chisels, high-grade tools *etc*.

3. **The open-hearth or Siemens-Martin process :** Steel is manufactured from cast iron in the open-hearth process. Steel-making by this process is carried out in a reverberatory-type furnace, whose hearth is lined with silica bricks in the case of *the acid process* for working with cast iron of little phosphorus-content, whereas the hearth is lined with calcined magnesia or dolomite in the case of *the basic process*, when cast iron containing appreciable amount of phosphorus is used. The furnace is heated by burning a mixture of producer gas and air. The furnace is provided with two heat regenerators, one at each side. The regenerators are structures of chequer brick-works, through which the producer gas-air mixture

and the hot products of combustion from the furnace alternately pass. The pre-heated mixture of producer gas and air is burnt over the furnace. The heat of the burning gas-mixture is used to pre-heat (about 500°C) the fuel in the regenerators, thus effecting economy in the fuel and rendering the maintenance of high temperature (about 1800°C) of the furnace possible.

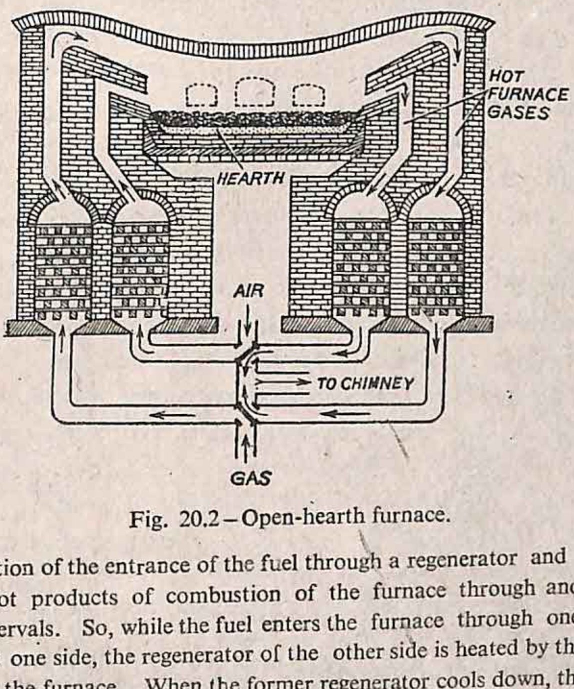


Fig. 20.2 – Open-hearth furnace.

[The direction of the entrance of the fuel through a regenerator and that of the exit of the hot products of combustion of the furnace through another can be reversed at intervals. So, while the fuel enters the furnace through one pre-heated regenerator at one side, the regenerator of the other side is heated by the outcoming hot gases from the furnace. When the former regenerator cools down, the directions of the fuel and hot gases are reversed, so that the fuel now enters through the heated regenerator and the hot gases come out through the cooled down regenerator.]

The charge of the furnace is mainly the cast iron (partly in the liquid state), delivered directly from the blast furnace, together with some iron or steel scraps and haematite. [Some limestone or lime is added in *the basic process*.] In the high temperature (~ 1800°C) of the furnace, the oxidising action of haematite (Fe_2O_3) oxidises carbon to CO and a part of sulphur to SO_2 which escape as gases. Phosphorus, silicon and manganese are converted into their oxides and form slag. [Phosphorus is eliminated only in the *basic process* as $Ca_3(PO_4)_2$ slag.] The remaining sulphur enters the slag as calcium sulphide.' The following reactions take place in the open-hearth process :

$Fe_2O_3+3C=2Fe+3CO\uparrow$; $2Fe_2O_3+3S=4Fe+3SO_2\uparrow$;
$5Fe_2O_3+6P=10Fe+3P_2O_5$; $P_2O_5+3CaO=Ca_3(PO_4)_2$ (*slag*) ;
$2Fe_2O_3+3Si=4Fe+3SiO_2$; $SiO_2+CaO=CaSiO_3$ (*slag*) ;
$Fe_2O_3+3Mn=2Fe+3MnO$; $MnO+SiO_2=MnSiO_3$ (*slag*).

The operation of eliminating the impurities as above in the open-hearth process takes about 8-10 hours. The molten mass on the hearth is then poured out into ladles by tilting the furnace and the upper layer of the slag is removed. Then a calculated amount of manganese is added in the form of ferro-manganese or *spiegeleisen* to the molten metal to remove sulphur as manganous sulphide (as slag) and for the deoxidation and re-carburization of the steel. A little aluminium or ferro-silicon is also added at this stage to remove last traces of dissolved gases in the product.

4. **The Bessemer process :** In this process, cast iron is de-carburised and the other impurities are removed by blowing air through the molten material (received directly from the blast furnace) in a large pear-shaped vessel called the *Bessemer converter*.

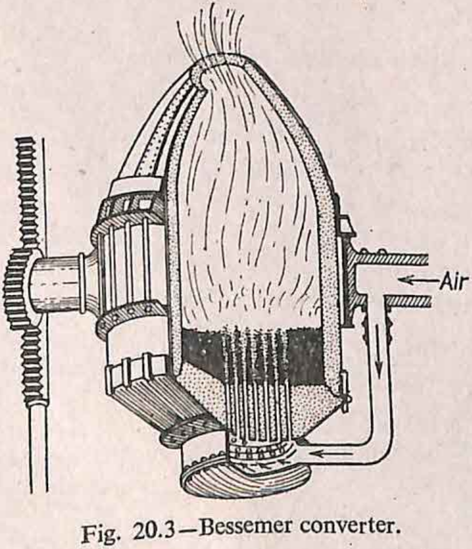


Fig. 20.3—Bessemer converter.

The converter is made of wrought iron plates rivetted together, with an inner lining and bed of silica and clay (or with refractory fire-bricks) in the *acid Bessemer process*. A wind-box is fitted at the bottom of the converted and the bed-lining is perforated into a number of inlets (similar to the *tuyeres* in the blast furnace) for blowing air under high pressure inside the converter. The converter is supported on two horizontal arms (called *trunnions*) in such a manner that it can be tilted in a vertical plane in any desired position for the convenience of receiving the charge, for blowing the blast of air and for pouring out the finished molten steel. In the *basic Bessemer process* (also known as *Thomas Gilchrist process*), the inner lining and bed of the converter are made of calcined dolomite, magnesia or lime. As in the open-hearth process, cast iron, containing little phosphorus, is worked up in the acid Bessemer process and that containing appreciable amount of phosphorus is treated in the basic Bessemer process.

In the actual operation, the converter is kept in the horizontal position, when molten cast iron from the blast furnace is directly transferred to it. The air-blast is then turned on and the converter is swung to the vertical position with continued air-blowing. At the temperature of the molten charge, the fine jets of air first oxidises silicon and manganese to their oxides which form a slag. Carbon of the cast iron is then oxidised to carbon monoxide and burns at the mouth of the converter with a blue flame and shower of sparks. The blue flame dies out as soon as the carbon is completely oxidised. The air-blast is then discontinued by tilting the converter again into the horizontal position. At this stage, the calculated amount of *spiegeleisen* or *ferro-manganese* (an alloy of iron and manganese with carbon) is added to the molten mass for the re-carburization of iron to obtain steel of desired quality. The blast of air is again turned on for a little while for proper mixing, and the molten steel is then poured into moulds. The whole operation requires about 10-15 minutes for completion and about 10-20 tons of iron can be processed in a single operation.

Ferro-silicon, ferro-vanadium, ferro-titanium alloys and some metallic aluminium are often added to the steel prepared by the above process as *scavengers* for removing dissolved gases (O_2, N_2, CO *etc.*) from the molten steel so as to eliminate any enclosed gas-bubbles in the steel-castings.

The following reactions take place in the acid Bessemer process: $2C+O_2=2CO$; $2CO+O_2=2CO_2$; $2Mn+O_2=2MnO$; $Si+O_2=SiO_2$; $S+O_2=SO_2$; $MnO+SiO_2=MnSiO_3$ (*slag*) ; $FeO+SiO_2=FeSiO_3$ (*slag*).

The operation procedures in the *basic Bessemer process* are almost similar to those of the *acid process*. As already stated, the inner lining and bed of the converter in this process are made of calcined dolomite and magnesia. Some lime is added to the charge for effective removal of phosphorus. The air-blast is continued here for a little more time after the sinking down of the blue flame of CO at the mouth of the converter to completely oxidise phosphorus. Phosphoric anhydride (P_2O_5) is formed by the oxidation of phosphorus, and this combines with the lime added to from a basic slag of $Ca_3(PO_4)_2.CaO$, which is removed before adding *spiegeleisen*. [The above basic slag is used as a useful fertilizer.]

Comparison between the open-hearth process and the Bessemer process : Both the processes utilize cast iron for the making of steel, but steel scraps can be used with cast iron in the open-hearth process, which is not possible in the case of the Bessemer process. Thus, the open-hearth process helps the disposal of large accumulation of scraps in the steel-industry. The Bessemer process is no doubt quicker and cheaper than the open-hearth process ; but cast iron of certain specified composition only is used in the Bessemer process, while the low-grade cast iron can also be worked up in the open-hearth process. The greatest advantage of the open-hearth process lies in the fact that, steel of much improved and superior quality can be prepared by this method, while the strict control of quality of the product is not feasible in the Bessemer process.

The Duplex process : This is a combination of the Bessemer process and the open-hearth process for the manufacture of steel. Here the rapidity of the Bessemer process is combined with the close quality control of the open-hearth process. In this process, the cast iron is first treated in the Bessemer converter to eliminate manganese, silicon and a part of carbon. The product, thus obtained, is further treated in the open-hearth process to eliminate carbon, phosphorus and some of the sulphur. Re-curburization with *spiegeleisen* is then effected in the usual manner. Tata steel plant at Jamshedpur makes large quantities of steel by this process.

The Lintz and Donawitz (L. D.) process : When steel is prepared in the Bessemer process by blowing air through molten cast iron, nitrogen (from the air) detereorates the mechanical properties of the product and badly affects the heat transfer in the mass inside the converter. These drawbacks have been overcome by the Lintz-Donawitz process, which is nothing but a modified Bessemer process. In this process, the converter has a basic lining of calcined dolomite or magnesia, and 95% pure oxygen is blown from above in a jet under very high speed inside the molten cast iron. At the high temperature attained during the process, almost all of the impurities (including phosphorus and sulphur) are eliminated. By controlling the oxygen-blast, the carbon-content in the product may be suitably fixed and the rapid control-analysis permits the keeping the silicon-content of the product at the desired level. The whole operation takes about 40-45 minutes for completion, and the quality of steel, thus produced, is much superior to that obtained by the Bessemer and the open-hearth process. The Rourkela Steel plant in India makes high grade steel by this process.

(5) The Electric furnace process or the Electrothermal process : Although it is possible by this process to prepare steel from cast iron, or even from pure haematite ore, its high cost and non-availability of cheap electricity in large quantities allow the processing of high quality steel only from the semi-finished products from the Bessemer or the open-hearth processes, or the production of special steels from steel scraps of known composition. The electric furnace, commonly used in this process, is of arc-type (Heroult furnace) and is made of heavy steel shell in the shape shown in the figure. It has a basic lining of calcined dolomite or magnesite. The roof of the furnace is made of fire-clay or silica bricks, through which stout graphite electrodes are introduced. The furnance is provided with a door for charging at one end and a spout at the other end to pour out the slag and the finished product by tilting.

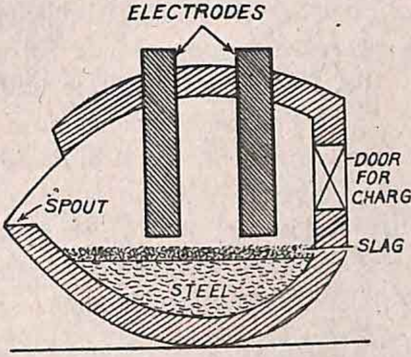


Fig. 20.4 – Heroult furnace.

The charge of semi-finished steel (from the Bessemer or the open-hearth process), with steel-scraps of known composition and some pure oxide ore of iron and lime, is introduced into the furnace through the charging door, so that some gap is maintained between the electrodes and the upper surface of the charge. A continuous arc is then struck between the electrodes and the charge by passing heavy alternating current of electricity through the water-cooled electrodes. The charge melts by the large heat generated by the arc. At such high temperatures, the added iron oxide oxidises impurities like silicon, manganese and phosphorus, which ultimately form slag of silicates of calcium, manganese and iron, together with calcium phosphate. Carbon is eliminated as carbon monoxide. The upper layer of the molten slag is separated from the lower molten layer of steel by pouring off through the spout of the furnace by tilting. A further charge, consisting of some lime, sand, fluorspar, petroleum coke, together with some ferro-silicon, is then added to the molten steel in the furnace to de-oxidise the steel by reducing any unreacted iron oxide. Iron oxide is first reduced ($Fe_2O_3+3C=2Fe+3CO\uparrow$) and sulphur (present as FeS) is then removed as calcium sulphide by reacting with lime : $FeS+CaO=CaS+FeO$. The FeO formed is readily reduced to metallic iron and more FeS from the steel enters into the reaction with lime, till the de-sulphurisation of steel is practically complete. The CaS produced floats on the surface of the molten steel and is removed as slag. The molten steel is then poured into moulds. The steel obtained by this process is almost free from S, P, any occluded gas-bubbles, and this may be re-carburized by adding requisite quantity of *spiegeleisen*, or special alloy-steels may be prepared from it by incorporating calculated quantities of the alloying metals as their ferro-alloys.

Steel of very high quality, as required for the fabrication of automobile engines, transmission systems, axles and wheels *etc*. is prepared by the electrothermal process. Accurate and desired composition of the steel can be attained by this proeess.

Properties of steel : Mild steel, containing a small proportion of carbon, is as soft and ductile as wrought iron. The ductility of steel decreases and its tensile strength increases with the increase of the amount of carbon in steel. Many of the useful physical properties of steel depend not only on its carbon-content, but on its *tempering* or *heat treatment*. When red-hot steel is quenched suddenly by plunging into water or oil, it becomes extremely hard but brittle. If the quenched steel is re-heated to different temperatures, ranging between 230°-300°C, and then cooled slowly, its properties are modified, depending upon the temperature of re-heating. This treatment is called *tempering or annealing* of steel. By adjustment of the temperature of tempering, different degrees of hardness and toughness can be imparted to steel to make it suitable for the production of various articles such as razor-blades, knives, chisels, saws, swords, axes, watch springs *etc*. The melting point of steel generally varies from 1300°-1500°C.

The special and alloy steels : Special or alloy steels are generally prepared in the electric furnaces from steel scraps, by adding some other metals to the molten mass. The alloying metals are commonly manganese, chromium, cobalt, nickel, molybdenum, vanadium, tungsten, titanium and silicon, which are added as their ferro-alloys. Often more than one of these metals are incorporated in the steel to develop certain special and useful properties in the products. Thus, alloy-steel containing about 2% Cr is very tough and such steel is generally used to prepare ball-bearings and armour plates. *Stainless steel* contains about 12-15% of Cr and it is resistant to corrosive action of weak acids. *Staybrite steel* contains about 18% of Cr and 8% of Ni, and it is resistant to the corrosive action of saline water (sea water). *High speed tool steel* contains Cr together with molybdenum or tungsten. This variety of alloy steel retains its hardness even at a red heat. *Chromium-vanadium steel*, containing about 1% of Cr and 0·15% of V, is very tough but ductile, and is used in autómobile industry and for making axles. Alloy steel, containing tungsten and/or cobalt, is used for making permanent magnets. *Nickel-chromium steel*, containing 3% of Ni, 0·5-1·5% of Cr and 0·3% of C, is used for making electric wires or cables, propeller shafts and parts of aeroplanes, motor cars and bicycles. Similar steel, containing higher percentage of Ni, is corrosion-resistant and is used for making motor engines. *Manganese steel*, containing about 10-14% of Mn, is very tough and is used for making stamping machines and jaws of crushers. A variety of *nickel-steel*, called **platinite**, contains about 42% of Ni, and it has the same thermal expansion as glass ; so platinite can be sealed in glass. Another variety of *nickel-steel*, called *Invar*, contains about 36% of Ni and 0·3% of C. It has negligible co-efficient of thermal expansion at ordinary temperatures and is used for making pendulums of clocks. *Silicon-steel*, containing about 3·5% of Si and very litle carbon, is used for making transformers and electromagnets. Another variety of *silicon-steel*, called *Duriron*, containing 15-18% of Si, possesses high resistance towards attacks by acids. It is, therefore, used for making pipe lines, pumps *etc*. for the conveyance of acids.

Pure Iron : Chemically pure iron, though of little practical use, may be prepared by electrolysing pure ferric chloride solution, or by reducing pure ferric oxide in a current of hydrogen at 1000°C. It is also obtained as a fine powder by the thermal decomposition of $Fe(CO)_5$ at 200 – 250°C : $Fe(CO)_5 = Fe + 5CO\uparrow$.

Properties of iron : Pure iron is a soft, bright and white metal, having a density of 7·85. It melts at 1530°C and boils at 2450°C. It is malleable and ductile, and is not hardened by quenching. The metal is attracted by magnet. It loses its ferromagnetism above 760°C. [Iron metal, prepared by heating the pure nitrate, carbonate or oxalate of iron in hydrogen, becomes pyrophoric.]

Allotropy of iron : Three different allotropic modifications of pure iron are known. These are *α-iron*, *γ-iron* and *δ-iron*, which are also known technically as *α-ferrite*, *γ-ferrite* and *δ-ferrite* respectively. The temperature ranges in which these three allotropes remain stable are different. They also differ in their hardness, crystalline from, magnetic property and also in their ability to dissolve carbon. These differences are tabulated below :

Property	*α-ferrite*	*γ-ferrite*	*δ-ferrite*
Temperature range of stability.	Upto 906°C.	906°-1404°C.	1404°C-1537°C
Hardness.	Soft.	Hard.	—
Crystal form.	Body-centred cube.	Face-centred cube.	Body-centred cube.
Magnetic property.	Strongly magnetic.	Non-magnetic.	Non-magnetic.
Power to dissolve carbon.	Nil.	Readily dissolves carbon.	Dissolves carbon.

As will be evident from the table, the transition of one allotropic form of iron to the other is represented by :

$$\alpha\text{-ferrite} \overset{906^\circ C}{\rightleftharpoons} \gamma\text{-ferrite} \overset{1404^\circ C}{\rightleftharpoons} \delta\text{-ferrite}$$

Carbon dissolves in iron, either to form a solid solution or a somewhat definite compound (carbide of iron). A solid solution of carbon in γ-iron is known as *austenite*. Again, molten iron, containing more than 4·3% of dissolved carbon, deposits a carbide of iron of the composition Fe_3C, known as *cementite*. An eutectoid mixture of cementite and α-iron has a pearly appearance and is known as *pearlite*. The characteristics of a sample of steel depend much on the relative amounts of austenite, cementite and pearlite in it.

Iron burns brilliantly and is oxidised when heated to red-heat in oxygen, and the ultimate product of oxidation is Fe_3O_4. The metal is also oxidised to Fe_3O_4, when super-heated steam is passed over red-hot iron : $3Fe+4H_2O \rightleftharpoons Fe_3O_4+4H_2\uparrow$. Iron combines directly with sulphur, phosphorus, halogens, carbon, boron and silicon at elevated temperatures. As the metal occupies a higher place than copper in the electromotive series, it displaces copper from a solution of a copper salt : $Fe+CuSO_4=FeSO_4+Cu\downarrow$. When iron powder is heated at 120°C under pressure in carbon monoxide, iron pentacarbonyl, $Fe(CO)_5$, is formed : $Fe+5CO=Fe(CO)_5$.

Iron dissolves in dilute HCl or H_2SO_4, with the liberation of hydrogen and the formation of the corresponding ferrous salts : $Fe+2HCl=FeCl_2+H_2\uparrow$; $Fe+H_2SO_4=FeSO_4+H_2\uparrow$. Various side-reactions occurs when the metal is heated with conc. H_2SO_4, and products such as ferric sulphate, SO_2, S *etc.* are formed. Very dilute HNO_3 reacts with iron in the cold to form ferrous nitrate and ammonium nitrate : $4Fe+10HNO_3=4Fe(NO_3)_2+NH_4NO_3+3H_2O$. With moderately concentrated HNO_3, however, ferric nitrate and nitrogen dioxide are formed : $Fe+6HNO_3=Fe(NO_3)_3+3NO_2+3H_2O$. The metal becomes inactive or *passive* on treatment with concentrated or fuming nitric acid. Iron does not react with alkalis at ordinary temperatures.

Passivity of iron : When a piece of iron is dipped in conc. HNO_3, it becomes *inactive* or *passive*. Such a piece of iron does not react with dil. acids, nor does it displace copper from the solution of the latter. This inertness of iron is known as **passivity**. This property of iron develops on dipping it not only in concentrated or fuming HNO_3, it is also caused by similar treatment with other oxidising agents such as chloric acid, chromic acid and iodic acid, as also by exposing it to dry NO_2 and by anodic oxidation of the metal. The passivity, however, is not equally enduring with all the agents mentioned. The passivity of iron can be removed by scratching, bending and hammering the metal, or by heating it in a current of hydrogen. Many theories were put forward from time to time to explain this behaviour of iron. The *oxide-formation theory*, however, seems to be the most appropriate among them. According to this theory, the passivity of iron is due to the formation of a very thin, colourless, adherent, continuous, invisible, transparent and amorphous superficial coating of iron oxide on the metal. This coating inhibits the normal chemical reactions of the metal. If by any method (such as those mentioned above), the surface-film of the oxide is broken, the metal exhibits its normal activities again. [A piece of passive iron may also be made active by making it a cathode in an electrolytic cell, or by touching it with a less noble metal (or a piece of normal iron) under a dilute solution of H_2SO_4.] The oxide-formation theory has been corroborated by isolating the transparent film of the iron oxide by dissolving out the inner portion of a piece of passive iron by a solution of iodine in potassium iodide.

Rusting of iron : Iron is not affected when exposed to dry air, but on exposure to ordinary (moist) atmospheric condition, it becomes covered with a reddish-brown amorphous crust (or scales) which is commonly known as *rust*, and the process as the *rusting of iron*. Very pure iron does not rust. The rusting of iron is a process of corrosion ; it depends upon the purity and homogeneity of the metal, and also on the external agents such as the presence of moisture, oxygen and any electrolyte. The chemical composition of rust is variable ; it is mainly the hydrated oxide of iron ($Fe_2O_3.H_2O$), often cotaminated with some carbonate of the metal. The association of iron with oxygen and liquid water (or sufficient quantity of moisture, such as, above 80% humidity in air) is a prerequisite for rust-formation. [It was thought earlier that CO_2 was necessary for the rusting of iron ; but, it has now been known that the presence of CO_2 is not essential for the process.]

The accepted mechanism of the rust-formation involves a complicated electrolytic process, in which anodic dissolution of iron takes place. The presence of impurities (or the non-homogeneous character) in a piece of iron and its non-uniformity of surface (*i.e.*, the existence of strain due to mechanical effect at different places) produce inequality between different parts of the same specimen and give rise to a difference of potential between these parts. On contact with moisture (or water), these parts are connected together to form and act as short-circuited voltaic cells. In the first step of the electrolytic process that follows, iron is oxidisied to ferrous ions at the anode and hydrogen gas (from water) is formed at the cathode :

Anode	*Cathode*
$Fe - 2e = Fe^{++}$	$2H_2O = 2H^+ + 2OH^-$
Iron dissolves.	$2H^+ + 2e = H_2$
	Hydrogen formed.

The Fe^{++} and the OH^- ions, produced in the action, combine into ferrous hydroxide, which forms ferrous carbonate with the CO_2 of the atmosphere : $Fe(OH)_2 + CO_2 = FeCO_3 + H_2O$. Ferrous carbonate is further oxidised by the oxygen of air to form ferric carbonate which is immediately hydrolysed by water to form hydrated ferric oxide or rust : $Fe_2(CO_3)_3 + H_2O = Fe_2O_3.H_2O + 3CO_2$. The fact that the formation of rust (or corrosion) of iron is retarded by alkali, finds logical explanation by the above mechanism, in that the formation of H^+ ions neccessary for the above electrolytic process is thereby hindered.

Rusting or other types of corrosion of iron is greatly increased by the acidic electrolytes such as metallic chlorides or sulphates, water containing organic acids due to decay of organic matter or even rain-water containing dissolved oxygen or acidic oxides such as CO_2, SO_2 *etc*. Corrosion is also effected by *differential aeration* of submerged iron articles (such as underground pipe lines), when their different parts are exposed to different concentrations of aerial oxygen. In such cases, the least aerated parts become anodic to the rest and electrolytic action, as described above, sets in. Corrosion is also caused by electric railway tracts and tram-lines due to stray currents.

Prevention of rusting :

Rusting (or corrosion) may be prevented by protecting the surface of the object by coating with metals (such as galvanising, sherardising, tinning, chromium or nickel plating) or with paints, coal tar, enamel *etc*. Production of a coating of Fe_3O_4 on the surface of the object also protects it from rusting. Oiling or greasing the surfaces may temporarily avert rusting of an iron article.

Uses of iron : As already stated, pure iron has got very little practical use, except in some scientific work. It is used for the preparation of certain compounds of iron and also as a reducing agent in conjuction with HCl. The uses of cast iron, wrought iron and different varieties of steel have already been enumerated while they were discussed.

COMPOUNDS OF IRON.

Although zerovalent iron occurs in the carbonyls such as $Fe(CO)_5$, $Fe_2(CO)_9$, $Fe_3(CO)_{12}$ *etc.*, and the hexavalency of the metal is attained in the *ferrates*, iron is predominantly di- and trivalent, forming the ferrous and the ferric compounds respectively. The ferrous salts are easily oxidised to the ferric salts and thus act as good reducing agents. [The hydrated ferrous ammonium sulphate, $FeSO_4.(NH_4)_2SO_4.6H_2O$ (Mohr's salt), however, is quite stable.] They produce almost colourless solutions, which are very little hydrolysed by water. Ferrous hydroxide is a quite strong base. Fe(II) salts, especially the sulphate, are isomporphous with the corresponding salts of bivalent metals like Co, Ni, Cr, Mn and Cu. The complex cyanide of bivalent iron, *viz.* $[Fe(CN)_6]^{4-}$ is a highly stable species.

Ferric salts, on the other hand, act as mild oxidising agents. Their aqueous solutions are considerably hydrolysed in water, so that the solutions give acid reaction. Ferric ion is colourless (or faintly violet) in solution, as is shown by the solutions of ferric salt of strong oxyacids (such as SO_4^{2-}, NO_3^-, ClO_4^- *etc*). The yellow or brown colour of the solutions of ferric halides and some other Fe(III) salts is due to the formation of colloidal ferric hydroxide by hydrolysis. Anhydrous ferric chloride and bromide are predominantly covalent compounds and are volatile. Ferric iron forms very strong complex cyanide ion, $[Fe(CN)_6]^{3-}$, and also strong complexes with phosphate, fluoride, tartaric acid, citric acid *etc.*

[The easy oxidation of ferrous salts is evident from the oxidation potential of the reaction, $Fe^{++} \rightarrow Fe^{+3}+e$; $E^\circ=-0{\cdot}771V$, which is such that even molecular oxygen can convert Fe(II) to Fe(III) in acid solution : $2Fe^{++}+\frac{1}{2}O_2+2H^+=2Fe^{+3}+H_2O$; $E^\circ=0{\cdot}46V$. Thus, in acid solution, ferrous salts quantitatively reduce permanganates and dichromates to Mn(II) and Cr(III) salts :

$$5Fe^{++}+MnO_4^-+8H^+=5Fe^{+3}+Mn^{++}+4H_2O\ ;$$
$$6Fe^{++}+Cr_2O_7^{2-}+14H^+=6Fe^{+3}+2Cr^{+3}+7H_2O.$$

In basic solution, the oxidation potential is more favourable :

$$Fe(OH)_2(s)+OH^-+\tfrac{1}{2}Fe_2O_3.3H_2O+e\ ;\ E^\circ=0{\cdot}56V.$$

So, ferrous hydroxide almost immediately turns dark (due to oxidation) when precipitated in presence of air.]

Oxides of iron : These compounds of iron are discussed together irrespective of the oxidation-states of the metal in them, mainly due to their tendency to become non-stoichiometric and because of the intimate relationship between their structures. Three oxides of iron are generally recognised, having composition FeO (ferrous oxide), Fe_2O_3(ferric oxide) and Fe_3O_4 (ferroso-ferric oxide).

Ferrous oxide (FeO) is obtained as black pyrophoric powder (*i.e.* spontaneously oxidised with incandescence by air), when ferrous oxalate is heated in air at 160° – 170°C, or when ferric oxide is reduced by heating in a current of hydrogen at 300°C. It is a basic oxide and dissolves in dilute acids to form ferrous salts :

$$FeC_2O_4=FeO+CO+CO_2\ ;\ Fe_2O_3+H_2=2FeO+H_2O\ ;$$
$$FeO+H_2SO_4=FeSO_4+H_2O.$$

Ferric oxide (Fe_2O_3) occurs in nature as the iron ore, *haematite*. It can be artificially prepared by igniting iron powder in air, or by heating the precipitated ferric hydroxide, $[Fe(OH)_3]$, the lower oxide, iron sulphates (both ferrous and ferric), ferric nitrate *etc.* :

$$2Fe(OH)_3=Fe_2O_3+3H_2O\ ;\ 4FeO+O_2=2Fe_2O_3\ ;$$
$$2FeSO_4=Fe_2O_3+SO_2+SO_3.$$

The colour of the products vary from yellow to red or dark violet (almost black). [The colour of the product obtained by strongly heating ferrous sulphate has a red colour, and it is used as a polishing powder or in cosmetic under the technical name, **rouge.**] When ferric oxide is heated to a very high temperature in air, it is transformed into ferroso-ferric oxide (Fe_3O_4). Ferric oxide prepared by heating at lower temperatures are soluble in dilute acids to form ferric salts ; but, strongly ignited Fe_2O_3 becomes insoluble even in concentrated acids. It is a weakly basic oxide (weaker than FeO) and that is why the ferric salts are considerably hydrolysed in aqueous solutions. The oxide, however, exhibits some amphoteric character and it forms ferrites when fused with alkalis :

$$Fe_2O_3+2NaOH=2NaFeO_2+H_2O\uparrow.$$

Ferric oxide is quite stable. It is reduced first to FeO and then to metallic iron when heated in a stream of hydrogen or carbon monoxide :

$$Fe_2O_3+H_2=2FeO+H_2O\uparrow\ ;\ FeO+H_2=Fe+H_2O\uparrow.$$

Ferroso-ferric oxide or triferric tetroxide (Fe_3O_4) : This is generally considered as the mixed $Fe^{II}-Fe^{III}$ oxide, which occurs abundantly in nature as black crystals of the mineral, *magnetite*. [It may also be regarded as ferrous ferrite.] It possesses a strong magnetic property and as such, is often known as the *magnetic oxide of iron*. [In ancient times, pieces of magnetite were used under the name *lodestone* for ascertaining true directions.]

Fe_3O_4 is obtained by passing super-heated steam over red-hot iron : $3Fe+4H_2O=Fe_3O_4+4H_2\uparrow$. [This reaction was earlier utilised in the manufacture of hydrogen.] The oxide is also formed by heating iron in air to redness, or by strongly heating Fe_2O_3 in vacuum. It melts at about 1540°C and is fairly resistant to the action of acids, hydrogen or chlorine. It is generally used for making electrodes in electrolysis and in arc lights.

[A hydrated form of this oxide, *viz*, $Fe_3(OH)_8$ or $Fe(OH)_2.2Fe(OH)_3$ is also known. A solution of this compound in HCl gives, on evaporation, crystals of $Fe_3Cl_8.18H_2O$. Similar bromide is also known. These are considered as the mixed halides of Fe(II) and Fe(III).]

FERROUS COMPOUNDS.

Ferrous hydroxide, [$Fe(OH)_2$], is formed as a white flocculent precipitate on treating a solution of a ferrous salt, in absolutely air-free condition, with alkali :

$$FeSO_4+2NaOH=Fe(OH)_2\downarrow+Na_2SO_4.$$

The white precipitate absorbs oxygen with the greatest avidity and turns to a dirty green mass which turns progressively darker, and ultimately changes to the reddish-brown ferric hydroxide. [The green product is supposed to be a basic ferrous ferrite, $(OH)Fe.O.Fe(OH)_2$. The intense colour of the product is typical of compounds which contain the same element in two different oxidation-states.] Ferrous hydroxide is a strong reducing agent. It dissolves in dilute acids to form ferrous salts, and in conc. NaOH solution to form sodium hydroxoferrate(II) : $Fe(OH)_2+2NaOH=Na_2[Fe(OH)_4]$.

Ferrous halides : All the four halides of bivalent iron, *viz*., FeF_2, $FeCl_2$, $FeBr_2$ and FeI_2 are known.

Ferrous fluoride (FeF_2) is obtained as colourless, relatively insoluble crystals of $FeF_2.8H_2O$, on dissolving iron in hydrofluoric acid and evaporating the solution. The anhydrous salt, also colourless, may be prepared by heating iron in hydrofluoric acid gas at high temperatures, or by heating the hydrated salt (or anhydrous ferrous chloride) in a stream of dry hydrogen fluoride.

Ferrous chloride, $FeCl_2$: The hydrated salt, $FeCl_2.4H_2O$, is obtained as a pale bluish-green crystals on concentrating a solution of iron in dilute HCl in absence of air. Other hydrates with 1, 2 and 6 molecules of water of crystallisation are also known. The anhydrous salt may be prepared as white shining flakes by passing a stream of dry HCl gas over red-hot iron powder (or, by heating ferric chloride in hydrogen, or by heating the hydrated salt in the absence of air). The compound is deliquescent in air and is highly soluble in water and alcohol. It melts at red-heat and volatilises at about 1000°C.

Ferrous bromide, $FeBr_2$, is obtained as an anhydrous yellow crystalline substance by burning excess of iron powder in bromine vapour. The hydrated variety, $FeBr_2.6H_2O$, is a green crystalline powder, which is obtained by strongly cooling a solution of iron in hydrobromic acid. When crystallised from solution above 45°C, the tetrahydrate, $FeBr_2.4H_2O$, is formed.

Ferrous iodide, FeI_2, is the grey product of the direct union on heating of the two components. At ordinary temperatures, iron gradually dissolves in water containing iodine ; from this solution, green crystals of $FeI_2.4H_2O$ are obtained on concentration in a desiccator. Higher hydrates are obtained on concentrating at low temperatures. Its solution is easily oxidised in air with the liberation of iodine. When heated to about 50°C, the hydrated salts or their solutions become black ; but, the original colour is regained on cooling.

Ferrous carbonate, $FeCO_3$, occurs in nature as **siderite** or **spathic iron ore.** It is formed as a white precipitate on adding a solution of an alkali carbonate to a solution of a ferrous salt : $FeSO_4 + Na_2CO_3 = FeCO_3\downarrow + Na_2SO_4$. The white precipitate, however, readily turns green on exposure to air and is finally transformed into reddish-brown ferric hydroxide. Ferrous carbonate dissolves in water saturated with CO_2 to form soluble ferrous bicarbonate, $Fe(HCO_3)_2$, by which hardness of water is often caused.

Ferrous nitrate [$Fe(NO_3)_2$] is formed in solution by the double decomposition between lead nitrate and ferrous sulphate solutions :

$Pb(NO_3)_2+FeSO_4=PbSO_4\downarrow+Fe(NO_3)_2$. The precipitated lead sulphate is filtered off and the filtrate, on evaporation in the cold, yields green crystals of the hexahydrate, $Fe(NO_3)_2.6H_2O$. It can also be prepared by dissolving iron filings in cold, dilute HNO_3. The salt is unstable and is readily decomposed.

Ferrous phosphate is formed as a colourless precipitate of $Fe_3(PO_4)_2.8H_2O$, on adding a solution of sodium phosphate to a solution of ferrous sulphate.

Sulphides of Fe(II) : Two sulphides of bivalent iron are known. These are : (i) the monosulphide, FeS and (ii) the disulphide, FeS_2. It should be noted that the metal in FeS_2 is *not* quadrivalent, but is actually bivalent, as has been shown by magnetic measurements. The bonding in the compound is very weakly ionic $[Fe^{++}(S_2)^{=}]$, the bonding forces involved are probably closely related in nature to the metallic bond.

Ferrous (*mono*) sulphide : This compound is prepared by melting powdered iron and sulphur together, or by heating iron filings in a stream of dry H_2S gas. [The substance is manufactured (for the generation of H_2S) by the first method, and the dark grey technical variety is invariably contaminated with unreacted iron.] It is also precipitated as a black product on passing H_2S gas through a solution of ferrous salt in presence of sodium acetate, or by adding ammonium sulphide solution to a ferrous salt solution.

Ferrous sulphide is practically insoluble in water, but it dissolves in dilute acids. The moist compound undergoes partial oxidation to ferrous sulphate on exposure to air.

Iron disulphide (FeS_2) is widely distributed in nature as the mineral, *iron pyrites*. It can be artificially prepared by boiling a suspension of FeS and S in water. The natural product is golden yellow in colour. It readily loses sulphur on heating and burns in air with the formation of ferric oxide and sulphur dioxide : $4FeS_2+11O_2=2Fe_2O_3+8SO_2$. It is insoluble in water ; but, the moist FeS_2 is slowly oxidised by atmospheric oxygen to produce ferrous sulphate and sulphuric acid : $2FeS_2+2H_2O+7O_2=2FeSO_4+2H_2SO_4$.

Iron pyrites is used as an important raw material for the production of sulphur dioxide in the manufacture of sulphuric acid.

Ferrous sulphate ($FeSO_4$) : The pale bluish-green, crystalline hepta-hydrate of ferrous sulphate, commonly known as *green vitriol*, is technically the most important salt of iron. [Fuming sulphuric acid or *the oil of vitriol* was formerly used to be prepared by the distillation of this compound and hence the name.] It is isomorphous with *white vitriol* or $ZnSO_4.7H_2O$ and *Epsom salt*, $MgSO_4.7H_2O$. Other hydrates of ferrous sulphate are also known. A pentahydrate, $FeSO_4.5H_2O$, isomorphous with *blue vitriol* ($CuSO_4.5H_2O$), is obtained by crystallising its solution in contact with a crystal of the latter. The heptahydrate is prepared by dissolving iron in dilute H_2SO_4 and evaporating the resulting solution or by adding alcohol to it. It is prepared on a large scale by weathering pyrites in moist air, whereby ferrous sulphate, along with free sulphuric acid is formed. The whole mass is leached with water and scrap iron is added. This reacts with the free sulphuric acid to produce ferrous sulphate and precipitate metallic copper from the cupric sulphate present in solution. Any ferric salt, present in the solution, is also reduced to the ferrous state. The liquid is filtered and evaporated to a small volume to crystallise ferrous sulphate heptahydrate.

Ferrous sulphate heptahydrate forms light bluish-green crystals (density=1·88), soluble in water. The crystals slowly effloresce in air and are superficially oxidised to brown basic ferric sulphate. The water of crystallisation are lost on heating (the last molecule is lost with much difficulty) to form the anhydrous salt as a white powder. This decomposes on stronger heating to form ferric oxide, sulphur dioxide and sulphur trioxide : $2FeSO_4=Fe_2O_3+SO_2\uparrow+SO_3\uparrow$. An aqueous solution of ferrous sulphate slowly oxidises in air ; the rate of oxidation is slower in acid solution than in neutral solution. Nitric oxide is absorbed by an aqueous solution of ferrous sulphate to form a brown addition-compound : $FeSO_4+NO=FeSO_4.NO$. It forms double salts with alkali sulphates or ammonium sulphate, and these are isomorphous with similar double sulphates of many bivalent metals. The double sulphate with ammonium sulphate is popular under the name of **Mohr's salt** and has a composition $FeSO_4.(NH_4)_2SO_4.6H_2O$. This is obtained as light bluish-green crystals on concentrating a mixture containing equimolecular proportions of $FeSO_4$ and $(NH_4)_2SO_4$. Mohr's salt is less soluble in water and is less readily oxidised by aerial oxygen than ferrous sulphate. It is largely used in volumetric analysis as a secondary standard.

Ferrous sulphate is used in the manufacture of ink and *Prussian blue* and also in dyeing, preservation of wood and sometimes in medicine. It also finds application as a fungicide.

FERRIC COMPOUNDS.

Ferric hydroxide, $Fe(OH)_3$, is thrown down as a brown gelatinous precipitate from a solution of a ferric salt on addition of ammonia or alkali hydroxide or carbonate : $FeCl_3+3NaOH=Fe(OH)_3\downarrow+3NaCl$; $2FeCl_3+3Na_2CO_3+3H_2O=2Fe(OH)_3\downarrow+6NaCl+3CO_2\uparrow$. In nature, hydrated ferric oxide, $2Fe_2O_3.3H_2O$, occurs as *limonite*.

Ferric hydroxide is insoluble in water, but soluble in acids to form ferric salts. It is converted to Fe_2O_3 on heating. Freshly precipitated ferric hydroxide is used as an antidote for arsenic-poisoning. Hydrated ferric oxide is used in the purification of coal-gas. Colloidal ferric hydroxide in used in medicine.

Ferric halides : Ferric fluoride, chloride and bromide are known, but the iodide is not formed due to the reduction of Fe^{+++} by the I^- ion.

Ferric Fluoride (FeF_3) is formed as the anhydrous salt (pale green or white) by passing fluorine gas over heated iron filings, or by heating dry Fe_2O_3 in a current of dry HF gas. The hydrated salt, $FeF_3.3H_2O$, is obtained as pale pink crystals by dissolving ferric hydroxide in hydrofluoric acid and concentrating the solution on water bath. The anhydrous salt is sparingly soluble in water. With alkali fluorides, this compound forms alkali ferrifluorides, M_3FeF_6 (M=an alkali metal). The complex FeF_6^{3-} ion is highly stable and is colourless in solution. This is the reason why Fe^{+3}-salts do not easily respond to the Prussian blue test in presence of an excecss of a soluble fluoride.

Ferric chloride ($FeCl_3$) : The anhydrous salt is most conveniently prepared by heating iron filings in a current of dry chlorine gas. The product sublimes and condenses in a cooled receiver as black scales (m.p. 300°C). The crystals vaporise at 280°C. The density measurement of the vapour indicates that ferric chloride is present almost entirely in the form of dimeric molecules, Fe_2Cl_6, at comparatively lower temperatures (around 400°C) ; but above 750°C, the density diminishes, corresponding to the formula

$FeCl_3$. The compound is also mono-molecular in alcoholic or ethereal solutions.

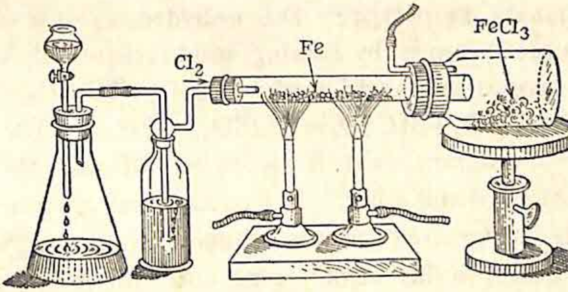
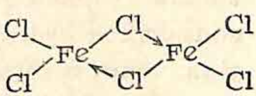


Fig. 20.5.—Preparation of anhydrous $FeCl_3$.

Anhydrous ferric chloride strongly absorbs moisture and fumes in moist air. It is highly soluble in water and alcohol, with the evolution of heat. The compound forms a number of hydrates, when crystallised from aqueous solution. The yellow ferric chloride crystals, ordinarily available, is the hexahydrate, $FeCl_3.6H_2O$. A solution of ferric chloride in water has a strong acid reaction due to hydrolysis : $FeCl_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + 3HCl$. The solution of the salt rapidly coagulates albumen.



Ferric chloride (dimer)

Ferric chloride is mainly used as an oxidant in organic dye-stuff industry and as a condensing agent and chlorine-carrier in organic synthesis. It is also used as mordant in dyeing.

Ferric bromide ($FeBr_3$) is prepared as reddish brown crystals by heating iron powder in bromine vapour. It resembles ferric chloride very closely. It decomposes into ferrous bromide and bromine on heating.

Ferric nitrate, $Fe(NO_3)_3$: The brown solution, obtained on dissolving metallic iron or ferric hydroxide is conc. HNO_3, deposits amethyst coloured crystals of $Fe(NO_3)_3.9H_2O$ on evaporation. It is highly deliquescent. The brown colour of the aqueous solution of the salt is attributable to hydrolysis : $Fe(NO_3)_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + 3HNO_3$. It is used in dyeing and in medicine.

Ferric phosphate, $FePO_4$, is obtained as a white substance of the composition $FePO_4.2H_2O$, on adding a solution of sodium phosphate to a ferric salt solution. The compound is insoluble in water.

Ferric sulphide, Fe_2S_3 : This is formed as a black substance when H_2S gas acts on ferric hydroxide, or when a solution of ferric chloride is mixed with a solution of colourless ammonium sulphide: $2FeCl_3+3(NH_4)_2S=Fe_2S_3+6NH_4Cl$. It is somewhat stable when dry, but in the moist state, it is readily oxidised by atmospheric air to Fe_2O_3 and S.

Ferric sulphate $Fe_2(SO_4)_3$: The anhydrous salt is obtained as a yellowish-white substance by heating solid ferrous sulphate or ferric oxide with conc. sulphuric acid: $2FeSO_4+2H_2SO_4\ \ Fe_2(SO_4)_3+SO_2\uparrow+2H_2O$; $Fe_2O_3+3H_2SO_4=Fe_2(SO_4)_3+3H_2O$. The mixture is cooled, the supernatant acid is decanted off and the product is washed with alcohol and ether. For commercial purposes, however, ferric sulphate is prepared only in aqueous solution, by oxidising a solution of $FeSO_4$ in dil. H_2SO_4 with conc. nitric acid: $6FeSO_4+3H_2SO_4+2HNO_3=3Fe_2(SO_4)_3+4H_2O+2NO\uparrow$. Ferric sulphate forms several hydrates, which cannot be easily isolated in the pure state. The hydrated salt can be made anhydrous by cautious heating; but, on stronger heating, the compound decomposes into ferric oxide and sulphur trioxide: $Fe_2(SO_4)_3=Fe_2O_3+3SO_3\uparrow$. Just like $Fe(NO_3)_3$, considerable hydrolysis of the salt takes place in the aqueous solution, which is turned reddish-brown. On boiling the aqueous solution, basic ferric sulphates of various compositions being formed. It forms double salts with alkali and ammonium sulphates.

Ferric sulphate is used in the manufacture of ferric alum and Prussian blue. It is also used as a mordant in dyeing and in medicine.

Ferric alums: The double salts of ferric sulphate with the sulphates of alkali metals or ammonium sulphate are known as ferric alums. They have the general composition, $MFe(SO_4)_2.12H_2O$ [or, $M_2SO_4.Fe_2(SO)_{43}.24H_2O$], where $M=NH_4$, Na, K, Rb, Cs. They form octahedral crystals, isomorphous with chromic and aluminium alums, and are soluble in water without undergoing any appreciable hydrolysis. Of the ferric alums, ferric ammonium and ferric potassium alums are technically important, and they are generally manufactured by oxidising a solution of ferrous sulphate (or a solution of metallic iron in dil.H_2SO_4) with conc. HNO_3 and crystallising after the addition of calculated amount of ammonium sulphate or potassium sulphate to it. Pure ferric alums form colourless crystals, but they may sometimes have pale violet (amethyst) colour due to the presence of manganese (III) sulphate as impurity. Ferric alums are used as mordants in dyeing industry and as a reagent (indicator) in volumetric analysis.

Ferric thiocyanate : The intense blood-red ccloration, developed on adding a few drops of a solution of a ferric salt to a solution of an alkali thiocyanate (or ammonium thiocyanate), slightly acidified with dil. HNO_3, has been attributed to the formation of hexathiocyanatoferrate (III) complex, $[Fe(SCN)_6]^{3-}$. This reaction serves as a very sensitive test for traces of ferric ion in solution. The colour is extractible in ether or amyl alcohol. The potassium salt, $K_3[Fe(SCN)_6].2H_2O$, can be isolated as deliquescent dark-red crystals. The complex is very weak and undergoes extensive dissociation when dissolved in water (and hence, the colour fades away on dilution). The solubility of the coloured species in organic solvent has prompted some chemists to hold that undissociated species $Fe(SCN)_3$ is formed in solution. Dark-red (almost black) crystals of $Fe(SCN)_3.3H_2O$ have also been claimed to have been isolated by evaporating the aqueous coloured solution. Some other chemists are of the view that the coloured species is the $[Fe(SCN)_2]^+$ ion. But, support to the formation of $[Fe(SCN)_6]^{3-}$ ions in solution has been given by the results of the transport experiment in alcohol solution. Ferric thiocyanate is decomposed by alkalis.

Ferrites and Ferrates : As already stated, Fe_2O_3 is an amphoteric oxide and it dissolves in concentrated alkali solutions to form alkali ferrites. [Powdered iron also slowly dissolves in very strong alkali solutions, with the liberation of hydrogen, to form ferrites : $2Fe+2NaOH+2H_2O=2NaFeO_2+3H_2\uparrow$.] Thus, sodium ferrite is obtained as green or red crystals by dissolving freshly precipitated $Fe(OH)_3$, or by fusing Fe_2O_3 with solid NaOH or Na_2CO_3 : $Fe(OH)_3+NaOH=NaFeO_2+2H_2O$; $Fe_2O_3+2NaOH=2NaFeO_2+H_2O$; $Fe_2O_3+Na_2CO_3=2NaFeO_2+CO_2\uparrow$. Sodium ferrite is decomposed by boiling water : $2NaFeO_2+H_2O=Fe_2O_3+2NaOH$. Ferrites of bivalent metals like Mg, Zn, Pb, Mn *etc.* are also known.

Although FeO_3 is unknown, the derivative of this hypothetical oxide, *viz.* the *ferrates*, are known. In these compounds, iron possesses a valency of +6 units and it occurs in the anion. The alkali ferrates may be prepared by heating iron filings with potassium nitrate, or by oxidising a suspension of freshly precipitated $Fe(OH)_3$ in alkali hydroxide solution with Cl_2 or Br_2. They are also formed during electrolysis of warm alkali hydroxide solutions between iron electrodes (preferably, cast iron) in a divided cell: $Fe+2KNO_3=K_2FeO_4+N_2\uparrow+O_2\uparrow$; $2Fe(OH)_3+10KOH+3Cl_2=2K_2FeO_4+6KCl+8H_2O$; $Fe+8OH^- - 6e=[FeO_4]^= +4H_2O$. The dark-red mass, obtained by fusing iron with nitre, is leached with water and the clear solution is made alkaline with KOH, when deep-red crystals separate out from the purple solution. The blood-red solution, obtained in the latter two methods of preparation, deposits deep-red crystals of the alkali ferrates on cooling to low temperatures.

Ferrates are isomosphous with chromates and manganates, as well as with sulphates. They are fairly stable in solution in presence of excess alkalis, but are rapidly decomposed on dilution or heating, with the precipitation of ferric hydroxide, accompanied by evolution of oxygen. Ferrates are very strong oxidising agents, even stronger than permanganates. They oxidise ammonia to nitrogen and chromic salts to chromates. When a ferrate solution is treated with dilute acids, oxygen is evolved and ferric salts are produced: $2FeO_4^{2-}+10H^+=2Fe^{+3}+\frac{3}{2}O_2+5H_2O$.

Iron Carbonyls (See also chapter XV of this volume):

Iron pentacarbonyl, $Fe(CO)_5$, is a light yellow liquid, having a high refractive index. It is formed by the action of carbon monoxide on finely divided iron at ordinary temperature and pressure; but, it is technically prepared by carrying out the reaction at 150°–200°C under pressure. The liquid boils at 109°C and freezes at –20°C. It is decomposed into metallic iron and CO on stronger heating. It is soluble in benzene and ether, but is decomposed by acids to form ferrous salts: $Fe(CO)_5+H_2SO_4=FeSO_4+H_2\uparrow+5CO\uparrow$. When exposed to light, the compound changes to the enneacarbonyl, $Fe_2(CO)_9$, with the evolution of carbon monoxide: $2Fe(CO)_5=Fe_2(CO)_9+CO\uparrow$. The valency of iron is taken to be zero in the pentacarbonyl.

Iron enneacarbonyl, $Fe_2(CO)_9$, is an orange coloured solid, insoluble in benzene and ether. It is formed, as already stated, by the photochemical decomposition of $Fe(CO)_5$. The orange coloured solid decomposes on heating to form $Fe(CO)_5$, with the liberation of CO and separation of metallic iron: $2Fe_2(CO)_9=3Fe(CO)_5\uparrow+3CO+Fe$. But, when heated at about 50°C in presence of toluene, the orange enneacarbonyl forms dark green crystals of trimeric tetracarbonyl, $[Fe(CO_4)]_3$. The green products decomposes on heating to CO and iron. The valency of iron is +3 in the enneacarbonyl.

Oxalates of Iron : Ferrous oxalate, $FeC_2O_4.2H_2O$, is obtained as a lemon-yellow precipitate on adding oxalic acid solution to a solution of a ferrous salt. The precipitate dissolves in an aqueous solution of potassium oxalate, and on adding alcohol to this solution, golden yellow crystals of the complex ferro-oxalate, $K_2[Fe(C_2O_4)_2].2H_2O$, separate out, This is a weak complex and its solution respond to all the usual tests of ferrous iron. The complex salt is used as a *developer* in photography.

On adding ammonium oxalate solution to a ferric salt solution, a brown precipitate of variable composition is formed. But, if excess ammonium oxalate solution is added, green crystals of the complex ammonium ferri-oxalate, $(NH_4)_3[Fe(C_2O_4)_3].3H_2O$, can be isolated from the solution. Other salts of ferri-oxalate are also known. When a solution of potassium ferri-oxalate is exposed to light, it passes to the ferrous state and CO_2 is evolved. [The trivalent iron oxidises oxalic acid to CO_2.] The extent of this reaction is proportional to the amount of light absorbed and as such, it is used in *actinometry* (for the measurement of quantities of light).

Complex Cyanides of Iron.

Although the simple cyanides of Fe(II) and Fe(III) cannot be prepared, the complex cyanides of the metal in both the oxidation states are well-known as stable compounds, in which the metal occurs in the anions with six coordinated cyano-groups. These are known as the **ferrocyanides,** $[Fe(CN)_6]^{4-}$, and **ferricyanides,** $[Fe(CN)_6]^{3-}$, according to their formation from the ferrous and the ferric ions respectively. The ferrocyanides and the ferricyanides are very stable complexes and do not give any usual test of iron or cyanide ions in aqueous solution. They are also not affected by HCl, HNO_3 or alkalis. Ferricyanides are strong oxidising agents, especially in alkaline medium, changing more or less readily into ferrocyanides, which are, therefore, more stable than the ferricyanides in alkaline solutions. Ferrocyanides, however, are easily oxidised in acid solution into ferricyanides (by suitable oxidants) and hence, are quite unstable in such media.

Ferrocyanides : Among the ferrocyanides, potassium ferrocyanide $K_4[Fe(CN)_6]$, is the most important compound. Ferrocyanides of many other metals are known, of which the alkali and alkaline earth ferrocyanides are soluble in water, while the others are insoluble.

Potassium ferrocyanide (*yellow prussiate of potash*) can be easily prepared in the laboratory by the action of excess of KCN solution on a solution of a ferrous salt, till the brown precipitate that is initially formed dissolves to give a clear yellow solution. The solution deposits yellow crystals of $K_4[Fe(CN)_6].3H_2O$ on concentration. [The compound can also be prepared in a similar way by dissolving iron filings in a solution of KCN.]

Potassium ferrocyanide is prepared on a large scale from the *spent oxide of iron*, obtained as a by-product in coal-gas industry. The *spent oxide* is boiled with slaked lime, when calcium ferrocyanide, $Ca_2[Fe(CN)_6]$, is formed in solution. The mixture is filtered and the clear filtrate is treated with potassium carbonate solution. Calcium carbonate is precipitated, which is filtered off. The filtrate, on evaporation, yields crystals of potassium ferrocyanide.

Potassium ferrocyanide, $K_4[Fe(CN)_6].3H_2O$ forms water-soluble yellow crystals which are quite stable in air. On gentle heating, the hydrated compound changes to colourless powder of the anhydrous salt. On stronger heating, it decomposes into potassium cyanide, iron carbide and nitrogen ; $K_4[Fe(CN)_6]=4KCN+FeC_2+N_2\uparrow$. On warming with dil. H_2SO_4, potassium ferrocyanide evolves HCN, but with the concentrated acid, carbon monoxide is formed :

$$2K_4[Fe(CN)_6]+3H_2SO_4=3K_2SO_4+K_2Fe[Fe(CN)_6]+6HCN\ ;$$

$$K_4[Fe(CN)_6]+6H_2SO_4+6H_2O=2K_2SO_4+FeSO_4+3(NH_4)_2SO_4+6CO\uparrow.$$

The compound is oxidised to potassium ferricyanide by oxidising agents like chlorine, potassium permanganate *etc.* :

$$2[Fe(CN)_6]^{4-}+Cl_2=2[Fe(CN)_6]^{3-}+2Cl^-.$$

It forms a deep blue precipitate of **Prussian blue** (with the formula $M^IFe[Fe(CN)_6]$, where M^I is Na, K or Rb) on reacting with excess ferric salts (See later).

Sodium ferrocyanide $Na_4[Fe(CN)_6].10H_2O$, is prepared as yellow crystals by methods similar to those of potassium ferrocyanide. **Silver and zinc ferrocyanides,** $Ag_4[Fe(CN)_6]$ and $Zn_2[Fe(CN)_6]$

respectively, are formed as white precipitates, and copper ferrocyanide, $Cu_2[Fe(CN)_6]$, as chocolate-brown precipitate, by the interaction of a solution of potassium ferrocyanide with solutions of silver nitrate, zinc sulphate and copper sulphate respectively.

The free **hydroferrocyanic acid,** $H_4[Fe(CN)_6]$, is a white crystalline substance which can be prepared by adding conc. HCl to a saturated solution of potassium ferrocyanide, followed by the addition of ether. It is soluble in water to form a strongly acidic solution. It is readily oxidised and partially decomposed in air to form Prussian blue.

Ferricyanides : The most important member of this class of compounds is potassium ferricyanide. Ferricyanides of some other metals are also known. Of them, the alkali and alkaline earth ferricyanides are water-soluble, while most of the others are insoluble in water.

Potassiam ferricyanide, $K_3[Fe(CN)_6]$, (*red prussiate of potash*) can be prepared by oxidising potassium ferrocyanide. The oxidation may be effected electrolytically, or chemically by using oxidising agents like Cl_2, Br_2, H_2O_2, permanganates *etc.* It is generally prepared by passing chlorine gas through an aqueous solution of potassium ferrocyanide : $2K_4[Fe(CN)_6]+Cl_2=2K_3[Fe(CN)_6]+2KCl$. The resultant deep red solution yields red crystals of potassium ferricyanide on concentration. The product is separated from KCl by repeated crystallisation from water.

Potassium ferricyanide is soluble in water. The aqueous solution is not very stable, as hydrolysis occurs. It is a strong oxidising agent, especially in alkaline media. It oxidises H_2S, SO_2, N_2H_4, bromides and iodides, and is itself reduced to ferrocyanide. Mutual reduction takes place when a solution of $K_3[Fe(CN)_6]$ is added to an alkaline solution of hydrogen peroxide : $2K_3[Fe(CN)_6]+H_2O_2+2KOH=2K_4[Fe(CN)_6]+2H_2O+O_2\uparrow$.

When a solution of potassium ferricyanide is added to solutions of silver nitrate, copper sulphate or lead nitrate, red coloured **silver ferricyanide,** $Ag_3[Fe(CN)_6]$, greenish brown **cupric ferricyanide,** $Cu_3[Fe(CN)_6]_2$ and brown coloured **lead ferricyanide,** $Pb_3[Fe(CN)_6]_2.16H_2O$ respectively are precipitated.

The free **hydroferricyanic acid,** $H_3[Fe(CN)_6]$, may be prepared as a brown crystalline substance by adding conc. HCl to a cold and saturated solution of $K_3[Fe(CN)_6]$.

Prussian blue and Turnbull's blue : When a solution of potassium ferrocyanide is added to a solution of a ferric salt (excess), a deep blue precipitate of the formula $M^{I}Fe[Fe(CN)_6]$, commonly known as **Prussian blue,** is formed. The precipitate is insoluble in HCl, and the reaction serves as a sensitive test of iron (III).

$$FeCl_3+K_4[Fe(CN)_6]=KFe[Fe(CN)_6]\downarrow+3KCl.$$

The compound is decomposed when boiled with alkali solutions to form ferric hydroxide and alkali ferrocyanide :

$$KFe[Fe(CN)_6]+3KHO=Fe(OH)_3\downarrow+K_4[Fe(CN)_6].$$

On heating with conc. H_2SO_4, Prussian blue decomposes with the evolution of carbon monoxide.

Prussian blue is used as a pigment.

In an identical manner, when a ferrous salt solution is added to a solution of potassium ferricyanide, a deep blue precipitate (known as **Turnbull's blue**) is formed. The precipitate is identical in composition and properties with the Prussian blue, and the X-ray analysis indicates that it is the same compound as the Prussian blue. [This happens due to the fact that ferricyanide oxidises the ferrous salt to the ferric state and is itself reduced to ferrocyanide in the course of the reaction and hence, the same compound as the Prussian blue is formed.]

On the other hand, if a solution of a ferrous salt is added to a cold and neutral solution of potassium ferrocyanide in complete absence of air, a white precipitate of potassium ferrous ferrocyanide, $K_2Fe^{II}[Fe^{II}(CN)_6]$, is formed. On contact with air, this substance readily changes to Prussian blue, $KFe[Fe(CN)_6]$.

Sodium nitroprusside, $Na_2[Fe(NO)(CN)_5].2H_2O$: This compound may be prepared by boiling sodium ferrocyanide with 50% HNO_3. It is, however, generally obtained as follows : potassium ferrocyanide is boiled with 50% HNO_3 and the solution cooled, when KNO_3 crystallises out. The crystals of KNO_3 are removed by filtration and the filtrate is neutralised with sodium carbonate. On concentrating the neutral solution, ruby-red transparent crystals of sodium nitroprusside are obtained.

Sodium nitroprusside is soluble in water and alcohol. It forms a deep violet solution of $Na_4[Fe(CN)_5NOS]$ with an alkaline solution of a sulphide or hydrosulphide, and the reaction serves as a test for their detection.

Tests : Iron salts can be detected by **the borax-bead test** or **the charcoal-block reduction test** in the dry way. Ferric salts form (i) a brown ppt. of $Fe(OH)_3$ on treatment with ammonia or alkali solns., (ii) a blood-red colour with ammonium thiocyanate soln., and (iii) a deep blue ppt. with potassium ferrocyanide soln. (Prussian blue). Ferrous salts give **Turnbull's blue test** with a ferricyanide soln.

Iron may be estimated gravimetrically by precipitating as $Fe(OH)_3$ and then igniting it to Fe_2O_3 and weighing. Volumetrically, it is estimated by titrating with a standard potassium dichromate or permanganate soln. after reducing previously to the ferrous state.

COBALT

Occurrence : Cobalt is a comparatively less abundant metal. Except the presence of the metal in very small amounts in meteoric iron, it is almost always available as minerals in combination with nickel and arsenic ; copper and iron are often associated with the ores of cobalt. [Some minerals of cobalt contain appreciable amounts of silver.] The principal ores of cobalt are *Smaltite* or *Speiss cobalt* ($CoAs_2$), *Cobaltite* or *Cobalt glance* ($CoAsS$) and *Erythrite* $[Co_3(AsO_4)]_2.8H_2O$. They are mainly available in Canada (Ontario province), Sweeden, Mexico, Morocco, Congo and North Rhodesia. Small quantities of cobalt ores are available in the Rajasthan state of India. Very small quantities of cobalt are present in soil and the metal is a constituent of Vitamin B_{12}.

Extraction : Cobalt is commonly extracted from *smaltite* and *cobaltite* ores. The powdered ore is at first concentrated by floatation process. The dried and concentrated ore is then roasted in air, when most of arsenic and sulphur are volatilised as As_2O_3 and SO_2, while iron is oxidised to iron oxide. The roasted ore is then mixed with sand and limestone, and the mixture is smelted in a small blast furnace in a current of air. The molten mass forms three distinct layers—(i) the upper layer consisting of slag of ferrous silicate and calcium silicate, (ii) the middle layer (called *speiss*) consisting of a mixture of molten arsenides of cobalt, nickel, copper, and iron and (iii) the lowermost layer (called *bullion*) containing easily reducible metals like copper and silver. The upper layer of the molten slag is rejected ; the bottom layer of *bullion* is processed for the recovery of silver by blasting air through the molten mass. The middle layer of *speiss* is separated, cooled and powdered. The powdered *speiss* is mixed with excess of NaCl, and the mixture is heated in a reverberatory furnace with a blast of air. Almost all of arsenic is volatilised in this process as As_2O_3 and the chlorides of cobalt, nickel, copper and iron are formed. [Silver is also converted into AgCl during the process.] The cooled mixture of the chlorides is extracted with hot water, when all the metal chlorides, except AgCl, pass into solution. It is filtered. [The remaining AgCl is separately dissolved in a solution of sodium thiosulphate or cyanide.] The filtrate is treated with some scrap iron, when copper is precipitated as metal. After the removal of precipitated copper, excess of calcium carbonate is added to the solution to precipitate all the iron as its hydroxide. Iron hydroxide is separated by filtration, and to the filtrate is added caustic soda solution, when cobalt and nickel are precipitated as their hydroxides. The combined hydroxides of cobalt and nickel are filtered, dried and ignited to obtain the mixture of the oxides of cobalt and nickel. The mixed oxides of cobalt and nickel are dissolved in HCl, and the solution is treated with calculated amount of lime and bleaching powder, so that only cobalt is precipitated as its hydroxide, but nickel remains in solution :

$$2CoCl_2+2Ca(OH)_2+Ca(OCl)Cl+H_2O=2Co(OH)_3+3CaCl_2.$$

The precipitated $Co(OH)_3$ is filtered, dried and ignited to form Co_3O_4. The oxide is then reduced to the metallic state by heating with charcoal or by reduction with hydrogen, or by the Goldschmidt's thermit process :

$$Co_3O_4+4C=3Co+4CO \; ; \; Co_3O_4+4H_2=3Co+4H_2O.$$

A very good method of separating cobalt from nickel is by precipitating the former as its ammine complex, $[Co(NH_3)_5Cl]Cl_2$.

Pure cobalt may be prepared by electrolysing a solution of cobalt sulphate ($CoSO_4$) in aqueous solution containing NH_4OH and $(NH_4)_2SO_4$.

Properties : Cobalt is a silver-white, lustrous, hard metal (density=8·7 ; m.p.=1499°C). It is malleable and ductile. Like iron, cobalt is also ferromagnetic. The metal is unaffected by aerial oxygen at ordinary temperatures. But, when heated in air strongly, it suffers superficial oxidation. Water has no action on metallic cobalt at ordinary conditions, but steam is decomposed by red-hot cobalt : $3Co+4H_2O \rightleftharpoons Co_3O_4+4H_2\uparrow$. The metal readily dissolves in dilute HNO_3, but slowly in dil. HCl or dil. H_2SO_4. Cold, fuming HNO_3 makes it *passive*. In the finely divided state, it can absorb a large quantity of hydrogen. At elevated temperatures, cobalt combines with sulphur, phosphorus and boron to form the corresponding binary compounds.

Uses : Cobalt is used for making valuable hard alloys for the preparation of cutting tools, drills, surgical instruments *etc.* Steel containing about 35% of cobalt is used for fabricating permanent magnets. The metal is used for cobalt-plating (similar to nickel-plating). Cobalt oxide is used for imparting blue colour to glass-wares and ceramics. Cobalt salts of some organic acids are used as *driers* in paints. Traces of cobalt have important biological action in animal and human systems. The radio-active isotope Co^{60} is used in the treatment of cancer and as a ready source of γ-radiation.

Alloys of Cobalt : Among the useful alloys of cobalt, mention may be made of **stellite,** which is a very hard and non-corroding alloy of cobalt, chromium and tungsten. It is mainly used for making surgical instruments, cutlery, high-speed tools *etc.* **Festel metal** or **cochrome** is an alloy of cobalt with iron and chromium. It is used for making cutlery and heating wires for furnaces (similar to *nichrome*). Cobalt steel, containing about 35% Co is used, as already stated, for making permanent magnets.

COMPOUNDS OF COBALT.

Cobalt usually exhibits bivalency in its simple salts, although a few stable simple compounds of tervalent cobalt are also known. But, in its complex compounds, the more stable species are generally formed by tervalent cobalt,—the complexes of bivalent cobalt being very easily oxidised to those of Co (III), especially in alkaline media. This phenomenon is a good example of the stabilization of unusual oxidation states of metals (Co^{+++} in these cases) through complex formation.

The aqueous solutions of cobalt (II) salts are generally pink in colour, which is probably due to the formation of the hexa-aquo ion, $[Co(H_2O)_6]^{++}$; the anhydrous salts are usually blue in colour. If excess of Cl^- ion is added to an aqueous solution of a cobalt (II) salt, its pink colour is changed to blue due to the formation of the chloro-complex, $[CoCl_4]^{2-}$:

$$[Co(H_2O)_6]^{++} + 4Cl^- \rightleftharpoons [CoCl_4]^{2-} + 6H_2O.$$

Cobalt (II) or cobaltous compounds.

Cobaltous oxide (CoO) : It is obtained as a pale olive-green powder by the thermal decomposition of cobaltous hydroxide, carbonate or nitrate in absence of air. It is a basic oxide and dissolves in acids to form cobaltous salts. On heating with the oxides of zinc, aluminium or magnesium, it forms the corresponding *cobaltiates* which have characteristic colours. [These are formed during the *cobalt nitrate tests* in the qualitative inorganic analysis. Zinc oxide form green zinc cobaltiate, $ZnCoO_2$ (*Rinmann's green*) ; aluminium oxide forms blue aluminium cobaltiate, Al_2CoO_4. (*Thenard's blue*) ; magnesium oxide forms grey mass, probably of magnesium cobaltiate, $MgCoO_2$.]

Cobaltous hydroxide, $[Co(OH)_2]$: On adding dilute ammonium hydroxide or sodium hydroxide solution to an aqueous solution of a cobaltous salt in absence of air, a blue precipitate is first formed. The colour of the precipitate slowly changes to pink on standing (but, rapidly on heating in basic medium). Both the precipitates are supposed to be of hydrated cobaltous hydroxide, having the composition $Co(OH)_2 \cdot \frac{1}{2}H_2O$, but with different crystalline forms. In the moist state, the hydroxide slowly obsorbs aerial oxygen and is transformed into brown Co_3O_4. It dissolves in strong alkali solutions to form a deep blue solution. With acids, it form cobaltous salts.

Cobaltous halides : All the cobaltous halides, *viz.* cobaltous fluoride, chloride, bromide and iodide, are known.

Cobaltous fluoride (CoF_2) : The anhydrous salt is obtained as a red powder, moderately soluble in water, by heating anhydrous cobaltous chloride in a current of dry HF gas. The hydrated salt, $CoF_2.4H_2O$, is generally prepared by dissolving cobaltous carbonate in an aqueous solution of hydrofluoric acid and crystallising the product by evaporation of the solution.

Cobaltous chloride ($CoCl_2$) : The anhydrous salt is formed as a hygroscopic pale blue substance on heating cobalt powder in a stream of dry chlorine gas, or by heating the hydrated salt, $CoCl_2.6H_2O$, in a current of dry HCl gas. The hexahydrate, $CoCl_2.6H_2O$, is generally prepared by dissolving the metal, its oxide or carbonate in hydrochloric acid and evaporating the resultant solution. It forms dark-red, deliquescent crystals which lose water on heating below 100°C to form the lower hydrates. At about 120°C, the hydrated salts become anhydrous with partial decomposition. The anhydrous salt is soluble in some organic solvents like alcohol, ether *etc.* to give blue solutions.

$$\underset{\text{(red)}}{CoCl_2.6H_2O} \xrightarrow{\text{heat}} \underset{\text{(pink)}}{CoCl_2.2H_2O} \xrightarrow{\text{heat}} \underset{\text{(pink)}}{CoCl_2.H_2O} \xrightarrow{\text{heat}} \underset{\text{(blue)}}{CoCl_2}$$

Cobaltous bromide ($CoBr_2$) : The dark green anhydrous salt is obtained by heating the powdered metal in bromine vapour, or by heating cobaltous oxide in dry HBr gas. The hydrated salts, $CoBr_2.6H_2O$ (reddish purple) and $CoBr_2.2H_2O$ (bluish purple) are also known. The anhydrous salt is very hygroscopic.

Cobaltous iodide (CoI_2) : The black coloured crystalline anhydrous salt is prepared by heating the metal in iodine vapour. The hydrated salt, $CoI_2.6H_2O$, is obtained as dark-red crystals on concentrating the red solution formed by the action of iodine and water on the powdered metal.

Cobaltous carbonate ($CoCO_3$) : When a solution of sodium bicarbonate, saturated with CO_2, is added to an aqueous solution of a cobaltous salt, in the cold, the pink coloured normal carbonate of Co(II) is precipitated. The salt is a hexahydrate, and forms double salts of the composition $M_2CO_3.CoCO_3.4H_2O$, where $M=Na^+$, K^+ or NH_4^+. Basic cobalt (II) carbonates are precipitated when only Na_2CO_3 or $NaHCO_3$ solution is added to a solution of a cobaltous salt.

Cobaltous nitrate [$Co(NO_3)_2.6H_2O$] is obtained as slightly deliquescent pink crystals by concentrating a solution of the metal, its oxide or carbonate in dilute HNO_3. Other hydrates with 9 and 3 molecules of water of crystallisation are also known. The hydrated salts cannot be made anhydrous by heating, as they are decomposed into Co_2O_3 at higher temperatures. The salt is soluble in water to give a pink solution.

Cobaltous sulphide (CoS) : The black precipitate of cobaltous sulphide is thrown down on adding a solution of ammonium sulphide or sodium sulphide to an aqueous solution of a cobaltous salt, or on passing H_2S gas through an alkaline (ammoniacal) solution of a cobaltous salt. The compound is insoluble in water and dilute acids, but is soluble in concentrated HCl, HNO_3 or aqua-regia. [It may be noted that cobaltous sulphide is not precipitated by passing H_2S through an acidic solution of a cobaltous salt (as in group II of inorganic analysis), but once CoS is precipiated from alkaline medium, it becomes insoluble in dil. acids.]

Cobaltous sulphate ($CoSO_4$) : This salt is obtained as its heptahydrate, $CoSO_4.7H_2O$, on dissolving the metal, its oxide or carbonate in dilute sulphuric acid and evaporating the resultant solution. The pink-coloured crystals of the heptahydrate is soluble in water. It is isomorphous with green vitriol ($FeSO_4.7H_2O$) and $NiSO_4.7H_2O$. Other hydrates of $CoSO_4$ are also known. The compound forms double salts of the composition $M_2SO_4.CoSO_4.6H_2O$, where $M=K^+$, Rb^+, Cs^+, NH_4^+ etc. These double salts are isomorphous among themselves and also with the corresponding double sulphates of Ni^{++}, Fe^{++}, Zn^{++}, Cd^{++} and Mg^{++}.

Cobaltous thiocyanate : When a strong ammonium thiocyanate solution is added to an aqueous solution of a cobaltous salt, a deep blue solution is formed. [The reaction is best carried out in presence of acetone.] From the blue solution, a blue-coloured complex thiocyanate of Co(II), *viz.* $(NH_4)_2[Co(SCN)_4]$, can be isolated by evaporation. The blue colour is extractible by ether or amyl alcohol and the reaction is often used to detect even minute amounts of cobalt.

Smalt : When oxides of cobalt are fused with K_2SO_3 and SiO_2 powder, a deep blue complex silicate of cobalt is obtained as a glassy product. This is known as *smalt*, and it is used as a pigment.

Cobalt (III) or cobaltic compounds : A very few simple cobaltic compounds are known. This is due to the fact that Co^{+++} is a highly powerful oxidising agent ($E^\circ=1.82$ v at 20°C) which oxidises even water, with the evolution of oxygen. In fact, all the simple cobaltic salts are very powerful oxidising agents.

Cobaltic oxide (Co_2O_3) : When a solution of a cobaltous salt is treated with a solution of an alkali hypochlorite or alkaline H_2O_2 solution, a black precipitate is obtained. The black compound is taken to be Co_2O_3 (hydrated) or cobaltic hydroxide.

Cobalto-cobaltic oxide (Co_3O_4) : This oxide is formed as a black powder when cobaltous oxide is strongly heated in air. Decomposition of cobaltous nitrate on gentle ignition also produces the oxide. It slowly dissolves in acids to form solutions of the corresponding cobaltous salts and liberating oxygen in the case of H_2SO_4 and chlorine in the case of HCl.

Cobaltic fluoride (CoF_3) : The anhydrous salt is obtained as a light brown powder by the action of fluorine on anhydrous cobaltous fluoride. The green coloured hydrated salt, $CoF_3.3{\cdot}5H_2O$, is deposited at the anode during electrolysis of a saturated solution of CoF_2 in conc. HF in the cold. The compound is unstable in aqueous solution, where it is hydrolysed into cobaltic hydroxide : $CoF_3+3H_2O=Co(OH)_3\downarrow+3HF$. Cobaltic fluoride decomposes into CoF_2 and F_2 on heating.

Cobaltic sulphate, $Co_2(SO_4)_3.18H_2O$: When a concentrated solution of cobaltous sulphate in $40\% H_2SO_4$ is electrolysed in a partitioned cell, anodic oxidation produces cobaltic sulphate which deposits as blue coloured needles on the anode. The compound is somewhat stable in solution in dil. H_2SO_4, but is immediately decomposed by water, with the evolution of oxygen and forming cobaltous sulphate : $2Co_2(SO_4)_3+2H_2O=4CoSO_4+2H_2SO_4+O_2\uparrow$. It forms alums with the sulphates of Na, K, Rb, Cs and ammonium. The alums have similar composition to and are isomorphous with potash alum, chrome alum and ferric alum. But, it is unstable and decomposes in aqueous solution with the evolution of oxygen.

COMPLEX COMPOUNDS OF COBALT.

Bivalent cobalt generally forms labile complexs which are susceptible to oxidation even by aerial oxygen. They should, therefore, be prepared in inert atmosphere. These complexes are either octahedral or tetratedral. [It fact, bivalent cobalt exhibits a greater tendency to form double salts.] On the other hand, tervalent cobalt, which form a few unstable simple salts, is known to produce innumerable complex compounds of very high stability with varieties of ligands. In fact, the number of cobaltic complexes much exceeds the number of known complexes of any other transition metal. The cobaltic complexes closely resemble the corresponding

Cr(III) complexes in many properties, although the former are somewhat more stable and more easily synthesized than the latter.

Tervalent cobaltic complexes may be either cationic, anionic or neutral in nature, and all of them generally have octatedral structures, the central Co^{+++} possessing coordination number six. Among the whole host of cobaltic complexes, the most important are the **cobaltammines**, the **cobalticyanides** and the **cobaltinitrites.**

Cobaltammines : Ligands like ammonia, amines (e.g. ethylenediamine) *etc.* have particular affinity for Co(III) and form strong complexes which are commouly classified as cobaltammines. These are generally prepared by oxidising the aquo Co(II) ion in solution by aerial oxygen or hydrogen peroxide (often in conjunction with a surface-active agent like activated charcoal) in presence of excess of the ligands. The most familiar examples are the hexammine salts, $[Co(NH_3)_6]X_3$, and the tris-ethylenediamine salts, $[Co(en)_3]X_3$, where X is one equivalent of an anion and *en*=ethylenediamine. The co-ordinated ligand molecules undergo slow exchange reactions and by gradual substitution of the amine ligand in the complex cations by negative atoms of groups, a series of new complexes with progressive variation in the charge of the complex ion may arise, forming ultimately the neutral complex :

$$[Co(NH_3)_6]^{+3}X_3 \rightarrow [Co(NH_3)_5X]^{+2}X_2 \rightarrow [Co(NH_3)_4X_2]^{+}X \rightarrow [Co(NH_3)_3X_3]^0$$

The neutral NH_3 molecules inside the co-ordination sphere may be replaced by other neutral ligands without altering the charge of the complex.

Cobalticyanides : On adding a solution of potassium cyanide to an aqueous solution of a cobaltous salt in the cold, a reddish-brown precipitate of cobaltous cyanide, $Co(CN)_2$, is first formed. This precipitate immediately dissolves on adding excess of KCN solution to produce a deep red solution. Red or light violet crystals of **potassium cobaltocyanide,** $K_4[Co(CN)_6]$, are obtained on adding alcohol to the deep red solution obtained above. Potassium cobaltocyanide is, however, very unstable, especially in solution, and is readily oxidised to **potassium cobalticyanide,** $K_3[Co(CN)_6]$, either on exposure of air or on boiling its aqueous solution :

$$4K_4[Co(CN)_6]+2H_2O+O_2=4K_3[Co(CN)_6]+4KOH\ ;$$
$$2K_4[Co(CN)_6]+2H_2O=2K_3[Co(CN)_6]+2KOH+H_2\uparrow .$$

Potassium cobaltocyanide thus acts as a strong reducing agent.

[It may be noted here that, while potassium ferrocyanide is more stable than potassium ferricyanide, the reverse is the situation in the cases of potassium cobaltocyanide and potassium cobalticyanide.]

Potassium cobalticyanide, $K_3[Co(CN)_6]$: An aqueous solution of potassium cobaltocyanide is boiled till the evolution of hydrogen ceases. The solution is then cooled and neutralised by adding acetic acid. The neutralised solution is evaporated to a small volume and alcohol is added to it in the cold. Almost colourless crystals of potassium cobalticyanide are obtained. These are filtered, washed with alcohol and dried air.

Potassium cobalticyanide is isomorphous with potassium ferricyanide and is highly soluble in water. It is a very stable complex and the aqueous solution does not give any test of cobalt or cyanide ions. The complex is also unaffected by HCl, HNO_3 or alkali solutions. On heating with conc. H_2SO_4, the compound is decomposed :

$$2K_3[Co(CN)_6]+11H_2SO_4+13H_2O=3K_2SO_4+2CoSO_4+6(NH_4)_2SO_4+11CO\uparrow+CO_2\uparrow .$$

The silver, lead or copper salts of cobalticyanide are obtained by the action of solutions of $AgNO_3$, $Pb(NO_3)_2$ or $CuSO_4$ to an aqueous solution of $K_3[Co(CN)_6]$. The free cobalticyanic acid, $H_3[Co(CN)_6]$, is a strong and stable acid which can be prepared as colourless crystals by removing the heavy metals by passing H_2S through a suspension of their salts in water, filtering of the precipitated metal sulphide and concentrating the resultant solution :

$$Cu_3[Co(CN)_6]_2+3H_2S=3CuS\downarrow+2H_3[Co(CN)_6].$$

Cobaltinitrites : Six mono-negative nitrite groups or ions are associated with a tervalent cobalt ion to produce the complex cobaltinitrite ion, $[Co(NO_2)_6]^{3-}$, possessing three negative charges or valencies.

Potassium cobaltinitrite, $K_3[Co(NO_2)_6]$: One of the important cobaltinitrite complexes is potassium cobaltinitrite which is known as **Fischer's salt**. It is prepared by treating a solution of a cobaltous salt with potassium nitrite solution in presence of acetic acid :

$$CoCl_2+7KNO_2+2CH_3COOH$$
$$=K_3[Co(NO_2)_6]\downarrow+2KCl+2CH_3COOK+NO\uparrow+H_2O.$$

The compound forms yellow powder which is sparingly soluble in water. It is quite stable in air and in presence of light. The compound is used as water-colour and also in oil-painting and for colouring porcelains. In the qualitative analysis, potassium is detected through the formation of potassium cobaltinitrite.

Sodium cobaltinitrite, $Na_3[Co(NO_2)_6]$: When a concentrated solution of cobaltous nitrate in 50% acetic acid is mixed with a concentrated aqueous solution of sodium nitrite at 45-50°C and a rapid stream of air is passed through the mixture, sodium cobaltinitrite is formed in solution. The compound is precipitated as a yellow powder on adding alcohol to the above solution : $Co(NO_3)_2 + 7NaNO_2 + 2CH_3COOH = Na_3[Co(NO_2)_6] + 2NaNO_3 + 2CH_3COONa + NO\uparrow + H_2O$. The compound is unstable in solution and decomposes with the liberation of oxygen : $2Na_3[Co(NO_2)_6] + H_2O = 6NaNO_2 + 2Co(NO_2)_2 + 2HNO_2 + \frac{1}{2}O_2$. The compound is used as a reagent for the detection of potassium.

Cobalt carbonyls : Two principal carbonyl complexes of cobalt are **cobalt tetracarbonyl, $[Co(CO)_4]_2$** and **cobalt tricarbonyl, $[Co(CO)_3]_4$**. [See also Chapter XIV of this volume.]

Cobalt tetracarbonyl is obtained as orange-red crystals when carbon monoxide reacts with powdered cobalt at 150-200°C under high pressure. The compound melts at 51°C.

Cobalt tricarbonyl is obtained as a black solid on heating the tetracarbonyl slightly above its melting point.

Tests of cobalt : In the dry test, cobalt is easily detected by the formation of blue colour of the borax bead in both oxidising and reducing flames. In the wet test, the metal is detected by the formation of yellow ppt. of potassium cobaltinitrite, when a solution of KNO_2 is added to a solution of its salt in presence of acetic acid. A very sensitive test of cobalt in solution is the formation of an intense blue colour on addition of a solution of ammonium thiocyanate to a solution of a cobaltous salt in presence of acetone (*Vogel's test*).

Cobalt is estimated gravimetrically by heating gently a cobalt compound with conc. H_2SO_4 and weighing as anhydrous $CoSO_4$. It is also weighed as Co_3O_4 by igniting at 800°C the ppt. of Co(III) complex of α-nitroso-β-naphthol. The electrodeposition of the metal from solution is also used for its estimation.

NICKEL

Occurrence : Nickel is found in nature in combination with sulphur, arsenic, antimony and silica and is invariably associated with cobalt. The principal ores of nickel are : (1) **Millerite, NiS ;** (2) **Niccolite** and **Kupfernickel, $NiAs_2$** and **NiAs ;** (3) **Pentlandite, (Ni, Fe, Cu)S ;** (4) **Ullmanite, NiSbS ;** (5) **Garnierite, (Ni, Mg) $SiO_3.H_2O$;** (6) **Smaltite,** (Fe, Co, Ni)As ; (7) **Nickel glance,** NiAsS. Of these, the most important are the sulphide-arsenide ores, available in appreciable quantities in the Sudbury district (Ontario, Canada) and the silicate ore (Garnierite) available in the silicate beds of New Caledonia (Australia). The Sudbury deposits constitute the main source of the metal. Nickel are also found in small quantities in Norway. In India, some nickel ores occur in Sikkim. Alloys of nickel with iron are found in meteorites.

Extraction : Nickel is generally extracted from the sulphide ore like *pentlandite*, or from the silicate ore like *garnierite*.

(A) **From sulphide ore :** The sulphide ore (Sudbury ore) is usually poor in nickel and contains not more than 3% of the metal. The powdered ore is first concentrated by the oil-floatation process, when the particles of the ore are collected in the froth which is skimmed off and the earthy gangue materials and other heavy impurities settle at the bottom of the tank. The concentrated ore contains about 25-28% Ni. It is roasted in a multiple-hearth furnace when most of the iron sulphide is oxidised to the oxide (with the elimination of SO_2), but nickel and copper sulphides remain practically unaffected. The roasted material is mixed with sand, coke and limestone, and is smelted in a small blast furnace with controlled air-blast. During this operation, iron sulphide is practically completely oxidised to iron oxide which reacts with silica to form a slag of ferrous silicate. Lime also combines with silica to form calcium silicate which, along with ferrous silicate, forms the upper layer of the molten mass, and beneath it lies the molten *matte* of copper and nickel sulphides, together with some iron. The upper layer of the slag is removed, the lower layer of the *matte* is taken in a Bessemer converter with basic lining, some silica is added and it is heated with hot air-blast. Here, most of the sulphur is oxidised to SO_2 and iron forms a slag of ferrous silicate. The slag is removed. The *matte* of copper-nickel sulphide at this stage contains about 56% Ni, 25% Cu, 14-17% sulphur and upto 0·5% iron. Copper and nickel may be separated from this *matte* either by (i) *the Orford process* or (ii) *the Mond process.* (i) *The Orford process* : In this process, the *matte* is melted with a mixture of coke and salt-cake (Na_2SO_4) in a furnace provided with basic hearth. Coke reduces Na_2SO_4 at the high temperature into sodium sulphide which dissolves practically the whole of cuprous sulphide and the solution remains in the upper layer of the molten mass, while the lower layer contains all the nickel as nickel sulphide. The upper layer of Cu_2S-Na_2S is removed and processed for the recovery of copper. The lower layer of nickel sulphide is solidified by cooling, crushed and washed with water to remove any adhering sodium sulphide. It is then roasted with NaCl to convert any copper sulphide present into the chloride which is extracted with water and removed. The residual mass is calcined with Na_2CO_3, washed with water and dried, when nickel oxide is obtained. The oxide is then reduced by strongly heating with charcoal powder or coke. In this process, gold, silver and platinum metals are obtained as valuable by-products. (ii) *The Mond's process* : This process is widely used for the separation of nickel from the Bessemerised matte of copper and nickel sulphides. The separation depends upon the fact that nickel forms a volatile carbonyl, $Ni(CO)_4$, when treated with CO at about 50-60°C, and the resultant carbonyl is decomposed into metallic nickel and carbon monoxide, when heated at about 180°C. Other metals in the matte, *viz*. copper or iron, do not form such carbonyls under the said conditions.

In actual practice, the matte of copper and nickel sulphides (containing a little iron) is roasted in a furnace whereby the oxides of the metals are formed. These are then heated to 350°C in a current of water gas, when the oxides of copper and nickel are reduced to the metallic state, but iron oxide remains unaffected. By the consumption of hydrogen during the above reduction, the employed water gas becomes enriched in carbon monoxide. The mixture of the reduced metal (along with a little iron oxide) is then passed down a tower called *volatiliser*, provided with shelves, and the CO-rich water gas is passed up from the bottom—the temperature of the tower being maintained at about 60°C. Under these conditions, metallic nickel alone combines with carbon monoxide to form the volatile tetracarbonyl, $Ni(CO)_4$, which, along with the spent water gas, is allowed to pass through the *decomposition tower*, maintained at 180°C. The tetracarbonyl is decomposed at the prevailing high temperature and the metallic nickel is deposited on the nickel pellets kept inside the tower : $Ni(CO)_4 \rightleftharpoons Ni + 4CO$. The liberated CO is pumped back into the volatiliser to transform fresh batches of metallic nickel into $Ni(CO)_4$. The metal obtained in this process is about 99·9% pure. The precious metals of the ores are retained in the volatiliser and may be recovered by suitable processes.

(B) **From silicate ores :** The crushed silicate ore, garnierite, is mixed with powder gypsum ($CaSO_4.2H_2O$) and coke. The mixture is smelted in a furnace, when the *matte* consisting of nickel and copper sulphides is formed. The major portion of iron in the ore is eliminated as ferrous silicate slag. The upper layer of the molten slag is removed and the lower layer of *matte* is oxidised in a Bessemer converted to produce oxides of copper and nickel. The oxides of the metals are then reduced by carbon into the metallic state. Nickel is finally separated from copper by the Mond's process. The following reactions take place in this metallurgy : $CaSO_4 + 4C = CaS + 4CO$; $CaS + NiSiO_3 = NiS + CaSiO_3$; $2NiS + 3O_2 = 2NiO + 2SO_2$; $NiO + C = Ni + CO$.

Electrolytic refining of nickel : Nickel extracted by any one of the above processes is refined electrolytically by depositing from a solution of nickel ammonium sulphate at 20-25°C. Blocks of the impure metal are used as the anode and thin polished pure nickel sheets are used as cathode. Silver, gold, platinum metals *etc*. are obtained in the anode slime after the electrodeposition of nickel.

Properties : Nickel is a hard, silver-white and malleable metal, with a specific gravity of 8·9. It melts at 1452°C and boils at 2730°C. The metal takes a high polish. It is magnetic below 340°C.

Nickel is not affected by air or oxygen at ordinary temperatures ; but, when heated in air (or oxygen), nickel (II) oxide is slowly formed. It does not react with water in the cold, but the powdered metal decomposes steam at red heat. Finely divided nickel absorbs large volume (about 17 times its own volume) of hydrogen. Nickel is very little acted on by dilute HCl and H_2SO_4 ; but, it dissolves in dilute HNO_3, concentrated HNO_3 renders the metal *passive*. Alkali solutions have no action on metallic nickel.

Uses : Nickel is used for making crucibles (for alkali fusion) and spatulas. Finely divided nickel is used as catalyst for hydrogenation of unsaturated organic compounds and also for hardening of fats and oils. It is an important constituent of many useful alloys (see below). The metal is used in electroplating (nickel-plating*) and in alkali accumulator cells.

Alloys of nickel : Many useful and important alloys of nickel are known. These are :

(i) **Nickel-steel :** It contains 2-5% Ni. Nickel-steel is very hard, rust-proof and possesses good elasticity. It is used in making protective shields, parts of automobiles and aeroplanes, heavy guns *etc*. *Invar* is a special type of nickel-steel which contains about 35%Ni, along with some manganese. Its co-efficient of expansion is very small and is used in making pendulums and other scientific instruments. Another variety of nickel-steel is known as *platinite*. It contains about 46% Ni and possesses the same co-efficient of expansion as glass, so that it can be easily sealed in glass (like platinum). It is used in electric bulbs and in radio-valves. *Permalloy* is an alloy of iron and nickel (containing 66-80% Ni and the rest Fe) which possesses high magnetic permeability.

(ii) **Copper-nickel alloys :** Alloys containing about 25% Ni and the rest copper are used in making coins, while those containing about 20% Ni are used in making jackets of bullets. An important copper-nickel alloy is **monel metal** which contains 67% Ni, 30% Cu and 3% (Fe+Mn). It is unaffected by high temperatures and is as tenacious as steel. **German silver** is an alloy containing 55% Cu, 20% Ni and 25% Zn. It is largely used in making household utensils and ornaments. **Constantan** contains 60% Cu and 40% Ni. It is used in making resistance wire and in thermocouples. **Platinoid** (60% Cu, 24% Zn, 14% Ni and a little tungsten) is used for similar purposes as constantan.

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* For nickel-plating iron articles, they are first coated with a thin layer of copper and then made the cathodes in the electrolytic bath of nickel ammonium sulphate at room temperature. Brass-articles are directly nickel-plated by using them as cathodes in the plating bath.

(iii) **Nickel-chromium alloy : Nichrome** (60% Ni, 15% Cr and 25% Fe) is an important alloy of this class. It has a high melting point and is used in making wries of heating coils.

COMPOUNDS OF NICKEL

Except one or two higher oxides, the simple compouds of nickel contain the metal in +2 oxidation state.

Oxides of nickel : Two oxides of nickel are known. These are (i) **nickelous oxide (NiO)** and (ii) **nickelic oxide** or **nickel sesquioxide, Ni_2O_3.**

Nickel (II) oxide or Nickelous oxide (NiO) : The compound is formed as a green powder, insoluble in water, on strongly heating nickel (II) hydroxide, nitrate or carbonate in absence of air. It dissolves in acids to form nickel (II) salts.

Nickelic oxide or Nickel sesquioxide (Ni_2O_3) : When nickel carbonate or nitrate is heated in air at about 300°C, nickelic oxide is formed as a black powder. The analysis of the oxide does not furnish a rigid composition of it and the results are often at variance with that required for Ni_2O_3. The black powder evolves Cl_2 and O_2 on dissolving in HCl and H_2SO_4 respectively.

When a suspension of nickel hydroxide in water is treated with chlorine or bromine, a black precipitate of hydrated nickelic oxide, $Ni_2O_3.H_2O$, is formed. As the compound contains larger amount of oxygen than that required for nickelic oxide, it has been suggested to be a mixture of Ni_2O_3 and NiO_2. The electrolytic oxidation of nickel hydroxide in a medium of strong KOH solution also gives similar product.

Nickel hydroxide, $Ni(OH)_2$: On adding an alkali solution to an aqueous solution of a nickel (II) salt, nickel hydroxide is precipitated as a light green gelatinous product. The precipitate becomes granular on heating for a long time. It dissolves in dilute acids to form solutions of nickel (II) salts. On dissolving it in ammonium hydroxide solution, complex nickelammine hydroxide is formed : $Ni(OH)_2 + 4NH_3 = [Ni(NH_3)_4](OH)_2$.

Nickel halides : All the four nickel halides, *e.g.* nickel fluoride, nickel chloride, nickel bromide and nickel iodide, are known, both as the hydrated salts as also in the anhydrous state. The anhydrous salts, except nickel fluoride, can be prepared by the direct interaction between the respective halogen and the finely divided metal at elevated temperatures. The hydrated salts are obtained by dissolving the oxide, hydroxide or carbonate of the metal in the corresponding hydrohalic acid and concentrating the resultant solution.

Nickel fluoride, NiF_2 : The anhydrous salt sublimes and forms, on cooling yellow crystals, on heating a mixture of nickel chloride and ammonium fluoride in a current of dry HF. The hydrated salt, $NiF_2.3H_2O$, is obtained by concentrating a solution of nickel carbonate or hydroxide in hydrofluoric acid. The compound is soluble in water.

Nickel chloride, $NiCl_2$, is obtained as green deliquescent crystals of the hexahydrate, $NiCl_2.6H_2O$, when a solution of nickel oxide, hydroxide or carbonate in dilute hydrochloric acid is evaporated. It is readily soluble in water, and the aqueous solution contains the complex hexa-aquo species, $[Ni(H_2O)_6]^{++}$. The crystals of the hexahydrate lose water on heating to about 70°C to form the tetrahydrate, $NiCl_2.4H_2O$. On stronger heating, it forms the basic chloride. The anhydrous salt sublimes and deposits as yellow scales on heating the dehydrated salt in a current of dry HCl gas.

Nickel bromide ($NiBr_2$) : The anhydrous salt is yellow in colour, while the hexahydrate forms green crystals. They are prepared by methods similar to those of the corresponding chlorides and have properties similar to the chloride.

Nickel iodide (NiI_2) : The anhydrous salt is black, while the hexahydrate is obtained as green crystals. The methods of prepartion and the properties of the compounds are similar to those of nickel chloride.

Nickel carbonate ($NiCO_3$) : On adding a solution of a calculated amount of sodium bicarbonate to an aqueous solution of a nickel (II) salt, an apple-green precipitate of $NiCO_3.6H_2O$ is obtained. If large excess of the precipitant is used, the double salt of the type $NaHNi(CO_3)_2.4H_2O$ is precipitated. The addition of an alkali carbonate solution to a solution nickel (II) salt precipitates the basic carbonate.

Nickel cyanide, $Ni(CN)_2$: When a solution of potassium cyanide is added (avoiding excess) to a solution of a nickel (II) salt, a green precipitate of hydrated nickel cyanide, $Ni(CN)_2.xH_2O$, is formed. The hydrated compound loses water when heated at 180—200°C to produce the yellowish brown anhydrous salt. The freshly precipitated hydrated nickel cyanide dissolves in excess of alkali cyanide to form a red solution containing the complex potassium nickelocyanide. On evaporating the red solution, yellow crystals of the complex salt, $K_2[Ni(CN)_4].H_2O$, are obtained. Potassium nickelocyanide is not susceptible to oxidation (difference from potassium cobaltocyanide), but is readily decomposed by acids.

Nickel nitrate, $Ni(NO_3)_2$: On dissolving metallic nickel or its oxide or carbonate in dilute HNO_3, a green solution of nickel nitrate is obtained. The solution gives green coloured crystals of the hexahydrate, $Ni(NO_3)_2.6H_2O$, on evaporation at ordinary temperatures. Crystallisation at higher temperatures yields the lower hydrates of the salt. The anhydrous compound is formed by heating the crystals of the hydrated salt in fuming HNO_3 : $Ni(NO_3)_2.6H_2O + 6N_2O_5 = Ni(NO_3)_2 + 12HNO_3$. Nickel nitrate is highly soluble in water.

Nickel sulphide (NiS) is obtained as a black precipitate on passing H_2S through an ammoniacal solution of a nickel salt (or by adding a solution of ammonium sulphide to it). Nickel is not precipitated as NiS when H_2S gas is passed through an acidic solution of a nickel salt ; but, once precipitated from the alkaline medium, NiS does not dissolve in dilute acids. It, however, dissolves slowly on heating with conc. HNO_3 or aqua regia.

Nickel sulphate ($NiSO_4$) : The heptahydrate of the salt, $NiSO_4.7H_2O$ (isomorphous with Epsom salt, $MgSO_4.7H_2O$), is obtained by dissolving the oxide or the carbonate of the metal in dilute H_2SO_4 and evaporating the solution at the room temperature. The green crystals of the heptahydrate are highly soluble in water. On heating, it gradually loses water to form the hexahydrate, tetrahydrate, dihydrate and ultimately the anhydrous salt at about 300°C. It forms double salts with ammonium sulphate and alkali metal sulphates. The double sulphates, $NiSO_4.M_2SO_4.6H_2O$ ($M = NH_4^+$ or alkali metal ions), are isomorphous with **Mohr's salt.**

Nickel ammonium sulphate finds useful application in nickel-plating.

Nickel carbonyl, $Ni(CO)_4$: This compound is formed when carbon monoxide is passed over finely divided reduced nickel at 40-50°C. [Higher temperatures, along with higher pressures are often used in the preparation.] It may be prepared in the laboratory by the action of carbon monoxide on nickel (II) phenyldithiocarbamate : $2Ni^{II}(S.\ SC.NH.C_6H_5)_2+4CO \rightarrow Ni(CO)_4+Ni^{IV}(S.\ SC.NH.C_6H_5)_4$.

Nickel carbonyl is a colourless, volatile, highly refractive, poisonous liquid (m.p. = −25°C ; b.p. = 43°C). It is easily oxidised by air and burns, when lighted, with a luminous flame. It is decomposed above 150°C to form metallic nickel and carbon monoxide. The compound is insoluble in water, but it dissolves in many organic solvents. Nickel carbonyl is not acted upon by dilute solutions of acids and alkalis. It reacts with chlorine to form $NiCl_2$ and $COCl_2$ (phosgene) : $Ni(CO)_4+5Cl_2=NiCl_2+4COCl_2$. Anhydrous HI reacts with it to produce NiI_2, CO and hydrogen : $Ni(CO)_4+2HI=NiI_2+H_2\uparrow+4CO\uparrow$. (For the structure of the compound, see chapter XIV).

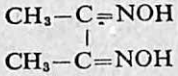
COMPLEXES OF NICKEL

Nickel forms large varieties of complex compounds in which the metal exists in different oxidation states, and also as a cation or an anion. The bivalent nickel mainly forms complexes where the co-ordination number of the metal is either 4 or 6. The complexes containing the tetracovalent metal are either planar or, sometimes, tetrahedral and those of the hexacovalent metal are, as usual, octahedral. [In the complexes of nickel with organic ligands, the metal is generally covalent.]

The mention of hexa-aquo complex ion, $[Ni(H_2O)_6]^{++}$ and the cyanide complexes, $[Ni(CN)_4]^{2-}$ have already been made. Tetrahalo complexes of the type $[NiCl_4]^{2-}$ are also known.

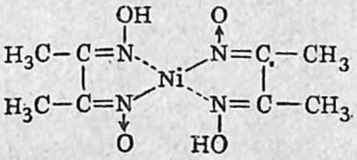
Nickelammines comprise most important and interesting class of complex compounds of nickel. When the green aqueous solution or a nickel salt is treated with excess of ammonia solution, a blue solution results. This solution, on concentration, deposits blue crystals of the nickelammines. Complexes of the type $[Ni(NH_3)_6]Cl_2$, $[Ni(NH_3)_4(H_2O)_2]SO_4$ *etc.* have been isolated. The complexes, containing diamines and polyamines as ligands, have also been isolated.

Tests : In the borax-bead test, nickel salts turn the bead reddish brown in the oxidising flame and grey (opaqe) in the reducing flame. A very sensitive test of nickel is carried out with the organic reagent, dimethyl glyoxime, which forms a bright red, silky precipitate with a solution of a nickel salt in slightly ammoniacal medium or in presence of sodium acetate.



$$\begin{array}{l} CH_3-C=NOH \\ \quad\;\;\; | \\ CH_3-C=NOH \end{array}$$

Dimethylglyoxime



Ni (II)-dimethylglyoximate

Estimation of nickel is generally made by precipitating the metal as nickel dimethylglyoximate in slightly ammoniacal medium, filtering off the red precipitate through a sintered glass crucible and drying the washed precipitate at 110°C. From the weight of the red ppt., the amount of nickel present in solution is calculated. [Dimethyl glyoxime is an excellent reagent which permits the detection and estimation of nickel (even in small quantities) in presence of many other metals, including cobalt.]

Other methods of detecting and estimating nickel in presence of cobalt : Nickel can also be detected and estimated in presence of cobalt by the following methods :

(i) A solution, containing both nickel and cobalt, is treated with an excess of KCN soln., when complex nickelocyanide and cobaltocyanide are formed. The mixture is then made alkaline with NaOH soln. and treated with Cl_2 or Br_2. Black hydrated nickelic oxide, $Ni_2O_3.H_2O$, is completely precipitated, leaving the whole of cobalt in solution. The ppt. is filtered and dissolved in acid and nickel is estimated as usual with dimethyl glyoxime.

(ii) A soln. containing nickel and cobalt is acidified with acetic acid and excess of potassium nitrate soln. is added to it. The whole of cobalt is precipitated as $K_3[Co(NO_2)_6]$ and nickel remains in solution. The ppt. of potassium cobaltinitrite is filtered off and washed well with water. Nickel is estimated in the combined filtrate and washings as usual.

MODEL QUESTIONS

INTRODUCTORY CHAPTER.

Essay-type :

1. Narrate briefly the development of chemistry through different ages.

2. Name the important branches of chemistry, describing briefly the scope of each of them.

3. Discuss Dalton's atomic theory in the light of the present-day knowledge of the structure of matter. What are the drawbacks of Dalton's theory and how should they be modified to explain correctly the nature of materials.

4. Discuss the limitations of the Laws of chemical combinations. Show clearly how these laws can be explained by Dalton's atomic theory.

5. Why do the common gases show deviations from the ideal gas equation ? How and why the ideal gas equation should be modified to explain the correct behaviour of the real gases.

6. (i) State Graham's law of diffusion. Deduce the mathematical relationship between the total pressure of a gas-mixture and the individual pressure (before mixing) of the consituent gases at a constant temperature.

(ii) Explain the term 'mole-fraction' of a constituent of a gas-mixture. Deduce the relationship between the partial pressure of a constituent gas and the total pressure of its mixture in terms of the mole-fraction of the former. What is the difference between 'diffusion' and '*effusion*' of a gas ?

7. What is the importance of 'Avogadro's hypothesis' in chemistry ? What led to its adoption ? Discuss a method of determination of the atomic weight of an element with the help of Avogadro's hypothesis. What is Avogadro's number ? Write down its value.

8. Describe in details a method for determining the accurate atomic weight on an element.

9. Enunciate 'Mitscherlisch's law of isomorphism' and show how this can be utilised in finding out the atomic weight of an element.

10. Discuss the phenomenon of '*isomorphism*' How would you recognise whether two substances are isomorphous or not ? Give examples in support of your statement. What is the difference between '*isomorphism*' and '*polymorphism*' ?

11. What is the difference between '*allotropy*' and '*polymorphism*' ? Give suitable examples. What are the different types of polymorphism ? Explain your answer with appropriate examples. What is '*isopolymorphism*' ?

12. Discuss the utility of the concept of mole in chemistry.

13. What are the various methods of determining the molecular weight of a compound ? Describe a method of determining the molecular weight of a volatile liquid, mentioning the precautions needed during the experiment and any apparent drawback of the method.

14. What methods are available for determining the molecular weight of a water-soluble non-electrolyte compound ? Describe one of the methods, showing the mathematical calculations involved.

15. What do you understand by the term 'limiting density of a gas or vapour' ? Explain clearly why the knowledge of limiting density of a gas (or vapour) is necessary for determining the correct molecular weight of a volatile substance.

16. Describe the effect of a non-volatile solute on (*a*) the freezing point and (*b*) the boiling point of a solvent. How are these effects influenced by the ionisation of the solute ?

17. Discuss the laws governing the normal effect which a solute has on the freezing point of a solvent. Indicate briefly the conditions which give rise to abnormal effects. When 0·3 gm. of a substance of molecular weight 150 is dissolved in 42 gms. of a certain solvent, the freezing point of the latter is lowered by 0·233°C. When 0·27 gm. of another substance is dissolved in 56 gms. of the same solvent, the observed depression of the freezing point is 0·218°C. Calculate the molecular weight of the second solute. [*Ans.* 108·2.]

18. When 0·22 gm. of a substance is vaporised in a Victor Meyer's apparatus, the volume of displaced air, collected over water at 20°C and 755 mm. pressure, is 46 ml. Calculate the molecular weight of the substance. [The aqueous tension at 20°C is 17·44 mm.] [*Ans.* 120]

19. Describe the method of determining the molecular weight of a non-electrolyte substance by the method of elevation of boiling point of its solution in a solvent. Calculate the molecular weight of a substance, if the boiling point of a solution of 3·7 gms. of it in 125 gms. of benzene is 0·44°C above that of pure benzene. [K_b for benzene=25·7° per 100 gms.] [*Ans.* 172·9]

20. Mention the conspicuous differences between a colloidal solution and a true solution. Discuss the important properties of a colloidal solution.

21. What are the different types of colloids ? Give examples. Mention the usefulness of colloids in industry and in our everyday life.

22. What factors influence the velocity of a chemical reaction and how ? Enunciate the law of mass action and find out the value of the equilibrium constant of a reversible reaction with its help. Explain the terms K_c and K_p and deduce their inter-relationship.

23. What are the effects of change in condition of the reaction on its equilibrium state ? Enunciate the guiding principle that predicts such effects. Discuss the physico-chemical principles involved in the manufacture of NH_3 by Haber's process and SO_3 by contact process.

24. Describe the phenomenon of catalysis. What different types of catalysis are recognised ? Give example of each type. What theories have been put forward to explain the catalytic action of substances ?

Short Answer type :

1. White short notes on : (a) Exothermic and endothermic reactions ; (b) Disproportionation reaction ; (c) Chain reaction ; (d) Inter-conversion of mass and energy ; (e) The limitations of the laws of stoichiometry ; (f) Van der Waals' equation ; (g) Joule-Thomson effect and its application ; (h) Diffusion and effusion of gases ; (i) Physical and chemical atomic weights ; (j) Mass-spectrographic method for determining atomic weight ; (k) Isomorphism, polymorphism, isopolymorphism and allotropy ; (l) Mixed crystals ; (m) Over-growth and parallel growth of crystals ; (n) Enantiotropy, Monotropy and Dynamic allotropy ; (o) Mole ;

(p) Limiting density ; (q) Abnormal vapour density of substances ; (r) Molal boiling point and freezing point constants ; (s) Solubility curves and their utility ; (t) Sols and gels ; (u) Coagulation of colloids and Hardy-Schulze rule ; (v) Protective colloid and gold number ; (w) Le Chatelier's principle ; (x) Homogeneous and heterogeneous catalyses ; (y) Biochemical catalysis and enzymes ; (z) Induced catalysis.

2. Explain, why (a) Hydrogen and helium are heated up when compressed at ordinary temperatures ; (b) The foul smell of H_2S gas is perceptible on just entering a laboratory, although the H_2S-Kipp is placed at the furthest corner of the room ;

(c) The solubility of sodium carbonate in water rises sharply upto 35°C and then gradually diminishes with the rise of temperature ; (d) Turbid water may be clarified by adding common alum ; (e) SO_2 can be liquified at ordinary temperature by applying high pressure ; (f) The molecular weights of compounds, determined by measuring their vapours at room temperature, are not accurate ; (g) A very small quantity of a catalyst should, theoretically, be sufficient to bring about the reaction of unlimited quantities of the reactants ; but, this is not true in actual practice ; (h) Colloidal As_2S_3 is readily precipitated by the addition of a small amount of $AlCl_3$, while larger amount of NaCl is required for the same precipitation.

Objective-type :

1. Fill up the blanks :

(a) The value of Avogadro's number is — .

(b) The value of *R* (gas constant) is — calories per degree (absolute) per mole.

(c) CO_2 is — compressible than H_2. (use *more* or *less*).

(d) The term '*b*' in the Van der Waals' equation is called — .

(e) A heavy gas diffuses at a — rate than a lighter gas. (use '*lower*' or '*higher*').

(f) The rate of diffusion of H_2 is — times that of oxygen.

(g) Red and yellow varieties of HgI_2 are examples of — . (use '*isomorphism*' or '*polymorphism*').

(h) Density of NH_4Cl vapour will — with the rise of temperature. (use '*increase*', '*decrease*' or '*remain same*').

(i) A mixture of 2 moles of H_2 and 1 mole of He occupies — litres at N.T.P.

2. Decide whether the following statements are **true** or **false** :

(a) Isomorphous substances must possess similar formula.

(b) Polymorphism and allotropy are similar phenomena.

(c) When a chemical reaction attains equilibrium, all the reactions stops.

(d) An exothermic reaction is favoured by the application of heat.

(e) As the use of a catalyst often produces good yield in a chemical process, it can change the state of equilibrium of a reaction forming a particular product.

(f) The equivalent weight of an element is invariable.

(g) Only ionic compounds dissolve in solvents like water.

(h) The number of molecules in 2 gms. H_2 and 71 gms. Cl_2 are the same.

(i) A Beckmann thermometer is used in the cryoscopic method to find out accurately the exact freezing point of the solution.

CHAPTER I : ATOMIC STRUCTURE.

Essay type :

1·1. Discuss the principles underlying (i) Thomson's method of determining e/m ratio for the electron and (ii) Millikan's method of determining the charge of the electron. Give the values of the electronic charge and mass.

1·2. What is the value of the charge on an α-particle ? Compare the value of the e/m ratio of an α-particle with that of a β-particle. What will be the value of the e/m ratio of a neutron ?

1·3 (a) Most of the atom is empty space.

(b) Most of the mass of the atom is concentrated at minute 'nucleus' placed at the centre of the atom.

(c) All the positive charge of an atom is located at the nucleus.

(d) Electrons, equal in number to the positive charge in the nucleus, are present in an atom.

(e) These electrons revolve round the nucleus in far away circular orbits with a velocity so that, the centrifugal force of circular motion is exactly balanced by the centrepetal force due to the attraction of positive nucleus on the negative electrons.

Justify each of the above statements in the light of the results obtained by Rutherford in his famous experiment on the scattering of α-particles by very thin metal foils.

1·4. What is the relation between the energy of a quantum of radiation and its frequency ? Give the numerical value of Planck's constant along with its dimensions. What is meant by *wave number* ?

1·5. What were the defects of the *nuclear atom* of Rutherford ? How did Bohr overcome those defects in his own model ?

1·6. State the postulates of *Bohr's theory of the hydrogen atom* and apply them to calculate the following :

(i) Radius of the first Bohr orbit.

(ii) The energy of the electron in the 3rd Bohr orbit.

(iii) Frequency of the radiation emitted when an electron jumps from the 3rd to the 2nd Bohr orbit.

1·7. State the defects of Bohr's theory of the hydrogen atom. How did Sommerfeld modify it ? How does Sommerfeld's theory help to explain the existence of fine structure of the hydrogen spectrum ?

1·8. Calculate the amount of energy required to remove an electron outside the influence of the nucleus from the 3rd orbit of the hydrogen atom. Calculate the circumference of the 4th Bohr orbit.

1·9. "Four quantum numbers are necessary to describe an electron." Name the four quantum numbers referred to above and explain their significance.

Short answer type :

1·10. (a) What is *Pauli's exclusion principle* ? (b) Show that, with the help of this principle it is possible to calculate the maximum number of electrons that can be accommodated in any shell designated by the principal quantum number *n*.

(c) Find the maximum number of electrons that can be accommodated in the N-shell.

1·11, State *Hund's rule of maximum multiplicity* and explain its significance with reference to the electronic structures of nitrogen (At. no. 7), silicon (At. no. 14) and chlorine (At. no. 17).

1·12 (a) Give the order in which the energy levels in an atom are filled with electrons. (b) Write the electronic configurations of the elements with the following atomic numbers : 3, 11, 8, 17, 24, 25, 29, 37, 56. (c) From these electronic configurations, write down the groups of the periodic table to which each of them belongs.

1·13. "The *azimuthat quantum number* tells us of the shape of the orbitals and the '*magnetic quantum number* gives their orientation in space". Illustrate this statement with suitable examples. Give the shapes of the s-and p-orbitals.

1·14. (a) Calculate the de Broglie wavelength of an electron travelling with 1×10^6 cms/sec. Given : $h = 6{\cdot}63 \times 10^{-27}$ erg-sec. and mass of the electron$=9{\cdot}1 \times 10^{-28}$ gm.

(b) Write down the Schrodinger wave equation for a small moving particle, like electron, existing in the field of the nucleus.

Objective type :

1·15. Answer by yes or no :

(a) Two electrons can have the same values for *n*, *l*, *m*, but different values of *s*.

(b) The electrons moving in fixed circular orbits have definite amounts of energy.

(c) The energy of the orbits increase with decrease in the value of the principle quantum number n.

(d) For a value of $n=4$, all the possible values of *l* are 0 and 1.

(e) The shape of an orbital is dependent on the azimuthal quantum number *l*.

(f) The s-orbitals are dumb-bell shaped and the p-orbitals are spherically symmetrical.

(g) The first three electrons in p-orbitals remain unpaired.

(h) Electrons spontaneously emit energy while moving in a stationary orbit.

(i) The phosphorus atom (at no. 15) has three unpaired d-electrons.

(j) Chromium has an electronic configuration of [Ar] $3d^4\ 4s^2$.

1·16. Fill up the blanks with correct words :

(a) There are — valence-shell elctrons in sulphur and the maximum valency of sulphur is —.

(b) The size of an orbital depends on the value of —, while the shape of an orbital is determined by the value of —.

(c) The angluar momentum of an electron revolving around the nucleus in a stationary orbit is given by the expression —.

(d) Transition of an electron from n=··· is called the Balmer series.

(e) Two electrons in a particular orbital must have — spin.

(f) For a value of $l=3$, m has values —.

(g) The number of electrons in chlorine is seventeen, its atomic number is —.

(h) No two electrons in an atom can have all four quantum numbers —. This is known as the —.

(i) The maximum number of electrons that can stay in a p-orbital is —, that in a d-orbital is — and that in a f-orbital is —.

(j) The region in space occupied by an electron is known as —.

(k) The electronic configuration of oxygen (at. no. 8) is —. It has — unpaired electrons.

CHAPTER II : PERIODIC CLASSIFICATION OF ELEMENTS.

Essay type :

2·1. What do you mean by the term *atomic number* ? "As a characteristic feature of an atom, *atomic number* is more fundamental than *atomic weight*"—Justify the statement in the light of Moseley's work on the characteristic X-ray spectra of the elements. Describe how the use of atomic number in place of atomic weight helped to overcome some of the anomalies of the original Mendeleyev periodic table.

2·2. "The actual electronic configuration, especially that in the valence-shell, is the fundamental feature on which the ideal periodic table should be based". Discuss and illustrate.

2·3. What is a *group* in the periodic table ? How do the more important properties like *atomic volume*, *ionization energy*, *electron affinity* and *electronegativity* vary within a group with the increase in atomic number ?

2·4. What is a *period* ? How do the above properties of the elements vary along a period as the atomic number increases ?

2·5. Explain the basis of classifying elements into four types or *blocks*. The *lanthanides* are accomodated in one position of the periodic table. Can we do the same for the *transition elements* ?

2 6. What is meant by the term ionization energy or ionization potential ? What are the factors on which its magnitude depends ? Discuss how it varies along a *period* and down a *group* with the increase in atomic number.

2·7. Explain why some elements have more than one ionization energies. In such cases, the 2nd ionization energy is always greater than the first ionization energy and the 3rd is invariably larger than the 2nd. Why ? "Highly charged monoatomic cations and anions are rare, but such polyatomic species are stable". Why ?

2·8. Define *electron affinity* and point out its physical significance. How does it differ from ionization potential ? The dinegative oxide ion, O^{2-} has a negative electron affinity, but we come across many stable ionic oxides. Explain why it so happens. (See Vol. II. p. 192). Explain why the electron affinities of the atoms increase from left to right of the periodic table.

2·9. What is meant by the term *electronegativity* ? State the physical basis of *Mulliken's electronegativity* and *Pauling's electronegativity*. Which one do you consider to be more useful and why ? How does Pauling's electronegativity vary across a period from left to right and down a periodic group ?

2 10. Define "atomic radius" of an element. Account for the variation of atomic radii (or atomic volume) from left to right of the periodic table. Explain why atomic radii increase down a group.

2·11. In the first series of transition metals, the atomic volume show very little change with the increase of atomic number. Why ? Explain the occurrence Lanthanide contraction. Why do Zirconium and Hafnium have very similar atomic volumes though their atomic numbers are widely different ? (Zr=40, Hf=72).

Short answer type :

2·12. "The radii of cations are invariably smaller than the corresponding atoms, while the radii of the anions are always greater." (a) Explain why it so happens, citing relevant examples. (b) Also explain why the radius of a dipositive ion is less than that of the corresponding monopositive ion.

2·13. Explain why there are small differences between the atoms of Cu, Ag and Au and their ions, compared to the large differences in the size of the alkali metals and their ions.

2·14. Indicate the regions of the periodic table where you will find the following : (a) metals, (b) non-metals, (c) elements with high electron affinity and high ionization potential, (d) elements with low ionization potential and large atomic volume and (e) zero electron affinity and very high ionization potential.

2·15. Which would be the larger ion in each of the following pairs ? V^{+2} and Fe^{+2} ; Mn^{+2} and Zn^{+2} ; O^{2-} and S^{2-} ; S^{2-} and Se^{2-} ; Fe^{+2} and Fe^{+3} ; Sn^{+2} and Sn^{+4}, Cl^- and Br^- ?

2 16. From the positions of the elements in the periodic table, predict the formula and nature of the compounds formed by (a) calcium and hydrogen ; (b) silicon and fluorine ; (c) carbon and silicon ; (d) potassium and bromine ; (e) aluminium and nitrogen ; (f) argon and fluorine.

Objective type :

2 17. Answer by **yes** or **no** :

(a) The Bohr periodic table is based on the electronic configuration of the elements.

(b) In the first transition series of elements, the 4d-orbitals are gradually filled up.

(c) The lanthanides are characterised by the presence of 4f-electrons.

(d) All the alkaline earth metals are characterised by a valence shell electronic configuration of ns^2.

(e) In the p-block elements, the differentiating electrons reside in the ns-level.

(f) Metals are good conductors of heat and electricity, while non-metals are non-conductors.

(g) The metals occupy the right side of the periodic table and the non-metals occupy the left side.

(h) The ionization potential increases with the increase in atomic radius.

(i) The ionization potential increases with the increase in nuclear charge.

(j) The screening effect of the different orbitals decrease in the order, s>p>d>f.

(k) The electron affinities increase from left to right of a periodic group.

(l) Electronegativity is the average value of ionization potential and electron affinity.

(m) The electron affinity of magnesium is lesser than that of Al and the electron affinity of sulphur is greater than that of selenium.

2·18. Fill up the blanks with appropriate words :

(a) The energy of a purely covalent bond in a molecule A—B, according to Pauling, is the——of the bond energies of the molecules A—A and B—B.

(b) The atomic radii of the elements of a particular periodic group increase with the——of atomic number.

(c) In the elements, where the last electrons are fed into the inner-f-shells, there is a contraction in volume. This is known as——.

(d) The radius of the chloride ion is——than that of the chlorine atom.

(e) The radius of the Ca^{+2} ion is——than that of the Ca-atom.

(f) In representative elements, oxidation state is governed by the tendency of the atoms to attain the most stable——configuration.

(g) Compared to the compounds of trivalent bismuth, pentavalent bismuth compounds are rather unstable and difficult to prepare. This happens because of the operation of——.

(h) Among a group of transition elements, the higher oxidation states become progressively——as we move down the group.

(i) In a period, the basicity of the oxides——and the acidity of the oxides——as we move from left to right.

(j) The metals of periodic groups IA and IIA form——hydrides while——hydrides are formed by most of the non-metals.

CHAPTER III : CHEMICAL BONDING AND THE STRUCTURE OF MOLECULES.

Essay type :

3·1. Why atoms at all undergo chemical reactions ? Why the inert gases do not form diatomic molecules ? What is a chemical bond ? Mention the different types of chemical bonds generally encountered. Explain the meaning of the terms 'electrovalence'. What are the chief factors on which the formation of an electrovalent linkage (or ionic bond) depends ?

3·2. Discuss the formation of an ionic bond in terms of energy decrease, and represent the formation of sodium chloride in terms of the *Born-Haber cycle*. What is the physical significance of the term *lattice energy* ? What elements are likely to form ionic bonds ?

3·3. Describe the important characteristics of ionic compounds. Why are the m.p.s and b.p.s of the ionic compounds so high ? Calcium chloride is highly soluble in water, but calcium fluoride is completely insoluble. Explain why it is so, in terms of lattice energies and solvation energies of $CaCl_2$ and CaF_2.

3·4. Explain the following : (a) NaCl is a better conductor of electricity in the molten state than in the solid state. (b) NaCl has a higher m.p. than $AlCl_3$, though its mol. wt. is less than that of $AlCl_3$. (c) Anhydrous $AlCl_3$ is covalent, but $AlCl_3.6H_2O$ is ionic. (d) AlF_3 is more ionic than $AlCl_3$. (e) In a series of ionic compounds, the bromides have higher b.p.s than the chlorides, but in a series of covalent compounds the reverse is true.

3·5. Explain clearly the meaning of the term 'covalence'. Describe the more important general properties associated with covalent bond. What elements are likely to form covalent bonds ?

3 6. Explain how two identical hydrogen atoms combine to form a hydrogen molecule. What is the source of energy of such a homopolar bond ? Explain clearly.

3·7. What makes a covalent compound polar ? What is the difference between a polar and a non-polar compound ? Are all covalent compounds non-polar ?

3·8. Discuss the formation of a sigma-bond and a pi-bond with suitable illustrations. Explain why a pi-bond is less stable than a sigma-bond. Show that a triple bond is made up of one sigma and two pi-bonds.

3·9. It is said that, usually, the number of unpaired electrons in the valence shell determines the covalence of an element. If this is so, how can you explain the tri-covalence of boron and tetra-covalence of carbon ?

3·10. What is meant by *hybridisation* ? How many types of hybridisation are possible involving s-and p-orbitals ? Give illustrations with diagrams. Give the disposition of the orbitals in sp^3d, dsp^2 and d^2sp^3 hybridisations.

3·11. Discuss the VSEPR theory of predicting the shapes of covalent molecules with relevant examples. Predict the shapes of the following species :

$BeCl_2$, BCl_3, PH_3, H_2S, H_2Se, NH_3, CCl_4, PBr_5, SeF_6, SF_6.

3·12. According to the electronic configurations of hydrogen, oxygen and nitrogen, the H_2O molecule should be linear and the NH_3 molecule should be plane triangular. But we find that both H_2O and NH_3 have distorted tetrahedral structure. Explain why it so happens.

3·13. Mention the important factors affecting bond lengths of covalent bonds, and illustrate the effects of resonance and hybridisation on bond lengths with suitable examples.

3·14. "When a cation and an anion are brought close to each other, the nature of the chemical bond between them will depend on the resultant effects of their mutual interaction." Explain and justify this statement by applying Fajan's rules.

3·15. Explain the following : (a) the m.p.s. of $NaCl > CaCl_2 > AlCl_3$; (b) m.p. of $MgCl_2$ is less than that of $CaCl_2$; (c) The m.p.s. decrease as $NaF > NaCl > NaBr > NaI$; (d) m.p. of $Cu_2Cl_2 <$ m.p. of KCl ; (e) m.p. of AgCl < m.p. of RbCl.

3·16. Explain what is meant by *hydrogen bond*. What are the two types of hydrogen bonds generally encountered ? Explain and illustrate the differences between the two. Explain the following : (a) the b.p. of H_2O is greater than that of H_2S ; (b) hydrofluoric acid forms bifluorides of the type KHF_2 but HCl can not do so ; (c) o-hydroxy benzoic acid is steam-volatile, but p-hydroxy benzoic acid is not ; (d) benzoic acid is a dimer in benzene.

Short answer type :

3·17. Explain the following: (a) Ammonia and organic amines co-ordinate with the halides of boron and silicon, but cannot do so with the halides of carbon. (b) $SiCl_4$ is hydrolysed rapidly by water but CCl_4 is not. (c) Nitrogen cannot form NF_5, but phosphorus easily forms PF_5. (d) SiF_4 reacts with HF to form H_2SiF_6, but CF_4 cannot form H_2CF_6.

3·18. (a) Explain the term *dipole moment* of a polar compound. In what unit is it generally expressed ? (b) Explain the trend in the change of dipole moment, HF>HCl>HBr>HI, observed in the case of halogen hydracids. (c) What structural and other information can you extract from the dipole moment data for the following molecules : CO_2=0·0D ; SO_2=1·6D ; H_2O=1·84D ; NH_3=1·46D ; CS_2=0·0D ; NF_3=0·2D ; NCl_3=0·8D.

3·19. "*Homolytic fission* of an electron-pair covalent bond takes place due to *electron unsharing* and leads to the generation of free radicals". (a) Explain and illustrate with relevant examples. (b) Mention some of the most important chracteristics of the free radicals.

3·20. Explain the terms (a) heterolytic fission, (b) carbanion, (c) carbonium ion, (d) electrophilic or anionoid reagents, (e) nucleophilic or cationoid reagents, giving suitable examples of each.

3·21. "*Inductive effect* represents a partial electron displacement of *permanent nature* along mutually connected covalent bonds, whereas, *electromeric effect* is a *transient but complete transfer* of a pair of electrons shared between two atoms differing in electronegativity." Discuss and illustrate with suitable examples.

3·22. Give a brief account of the different types of *dipole bonds*.

Objective type :

3·23. Answer by yes or no :

(a) Ionic compounds are formed between elements of groups widely separated from each other in the periodic table.

(b) No separate molecules are present in the crystal lattice of an ionic compound. It exists in an almost non-ending array of oppositely charged ions.

(c) Ionic compounds dissolve in non-polar solvents.

(d) Whether an ionic solute will dissolve in a particular polar solvent depends on the relative values of the lattice energy and the solvation energy with respect to the solute-solvent pair.

(e) BF_3 and BCl_3 are electron-deficient compounds.

(f) The octet rule is strictly obeyed by the elements of the two short periods, but the elements of the long period can expand their octet upto twelve electrons.

(g) Nitrogen in ammonia and oxygen in water have one and two lone pairs respectively.

(h) The structure of NO can be fully explained by the presence of normal electron-pair covalent bonds.

(i) The formation of the ammonium ion is the result of a donor-acceptor interaction between NH_3 and H^+.

(j) Repulsion between different types of electron-pairs in a molecule follow the trend, lone-pair : lone-pair$>$lone-pair : bond-pair$>$bond-pair : bond-pair.

3·24. Fill up the blanks with appropriate words :

(a) The energy released when one formula-weight of an ionic crystal-lattice is formed by the regular arrangement of a requisite number of anions and cations in a definite pattern, is termed as the —.

(b) The value of the lattice energy U, can be calculated from the Born equation —.

(c) The energy required to break ionic bonds present in one formula-weight of an ionic compound is called the —.

(d) $CaCl_2$ is highly soluble in water, but CaF_2 is insoluble. This is because the — energy of CaF_2 exceeds the — energy of the Ca^{+2} and $2F^-$ ions, while the — energy of Ca^{+2} and $2Cl^-$ ions exceeds the — energy of the $CaCl_2$.

(e) The stability of the hydrogen molecule-ion is due to — between two equivalent structures.

(f) The properties of the NO_2 molecule can be explained by the presence of one — bond in it.

(g) The binding energy of a homopolar or covalent linkage is derived from a — process between two or more states of equal energy.

(h) The structure of an AX_2-type molecule will always be linear.

(i) All AX_3-type molecules are plane-triangular in shape.

(j) The m.p.s. and b.p.s. of covalent compounds are generally — than that of ionic compounds.

(k) The covalent bond has definite — character and this is why they have definite — and structure.

(l) SF_6 has — structure.

3·25. Tick the correct answer :

(a) The shape of the PH_3 molecule is (i) tetrahedral, (ii) linear, (iii) plane triangular, (iv) distorted tetrahedral.

(b) The H–N–H angles in ammonia are (i) 104°31, (ii) 109° 28′ (iii) 120° (iv) 93°20′.

(c) The type of hybridisation involved in the acetylene molecule is (i) dsp^2, (ii) sp^3, (iii) sp, (iv) sp^2.

(d) The ethylene molecule possess (i) 3 sigma and 3 pi-bonds, (ii) 5 sigma and 1 pi-bonds (iii) 4 sigma and 2 pi-bonds.

(e) Zero dipole moment is exhibited by (i) BCl_3, (ii) H_2O, (iii) $CHCl_3$ and (iv) CO_2.

(f) dsp^3-hybridisation results in (i) square pyramid, (ii) trigonal bipyramid, (iii) octahedral shape.

(g) Highest value of dipole moment is shown by (i) HCl, (ii) HI, (iii) and HF.

(h) The shape of the $Ni(CO)_4$ molecule is (i) square planar, (ii) pyramidal, (iii) tetrahedral, (iv) square pyramidal.

(i) AlF_3 is ionic but $AlCl_3$ is covalent. This can be explained on the basis of : (i) lattice energy, (ii) Fajan's rule, (iii) resonance, (iv) crystal structure,

(j) The force of attraction in gaseous HCl is a (i) dipole-dipole type (ii) dipole-induced dipole type, (iii) hydrogen bond type.

(k) The shape of the H_2S molecule is (i) linear (ii) angular (ii) square planar.

(l) A homolytic fission of an electron-pair covalent bond between carbon and another atom leads to the formation of (i) carbonium ions, (iii) free radicals.

(m) A carbonium ion is (i) an electrophile (ii) a nucleophile.

(n) The inductive effect is a (i) temporary, (ii) complete transfer of a pair of electrons.

(o) High charge on the cation and the anion favours (i) electrovalent character (ii) covalent character.

(p) Small cation and large anion induces (i) covalent character (ii) ionic character in a compound.

(q) When the number of valence electrons in the combining atoms are less than the valence-orbitals in them, the bond between the two combining atoms become — in character.

(r) H_2S is a gas but H_2O is a liquid. This can be explained on the basis of : (i) molecular weights of H_2O and H_2S, (ii) hydrogen bonding (iii) Fajan's rules.

CHAPTER IV : THE NUCLEUS AND THE PHENOMENON OF RADIOACTIVITY.

Essay Type :

4·1. (a) Name the more important fundamental constituents of the atomic nucleus (also known of nucleons) along with their conventional symbols.

(b) Define and illustrate *mass defect.*

4·2. Explain the term *binding energy* and state its relation with *mass defect*. In what unit is it usually expressed ? What is *packing fraction* ?

4·3. Define binding energy per nucleon. Draw a plot of binding energy per nucleon as a function of mass number. What conclusions can be drawn by the careful analysis of the different regions of the curve ?

4·4. "It has been established that the nuclear attractive forces are quite different from either gravitational or electrostatic forces with which we are familiar." Discuss the special characteristics of the nuclear forces. How does the *meson theory* explain the existence of nuclear binding forces ?

4·5. Examine the plot of number of neutrons against the number of protons (as found in the case of the elements of the periodic table) and explain the possible modes of decay of (i) the elements lying above the line representing n : p=1 and (ii) the elements lying below this line.

Predict the modes of decay of the following nuclei : ${}_6C^{13}$, ${}_6C^{14}$, ${}_7N^{15}$, ${}_5B^{8}$, ${}_1H^{3}$, ${}_{15}P^{30}$, ${}_{16}S^{34}$, ${}_{14}Si^{27}$, ${}_7N^{13}$, ${}_{18}Ar^{40}$.

4 6 (a) Define and illustrate the following : isotopes, isobars, isotones and isomers (nuclear).

(b) Name the more important methods of separating isotopes of elements. Describe the principles of the method of *thermal diffusion* and the *electromagnetic* method (mass spectrographic method) of isotope separation.

(c) What is *separation factor* ? Has it any physical significance ?

(d) The ${}_8O^{16}$ isotope is chemically identical with the ${}_8O^{18}$ istope. Why ?

4·7. (a) How was the phenomenon of radioactivity discovered ?

(b) What different types of radiations are emitted by radioactive substances. Describe some important characteristics of these radiations.

(c) How can they be distinguished from each other ?

4·8. Briefly outline the experimental basis of the theory of radioactive disintigration proposed by Rutherford and Soddy. Derive a mathematical expression for the disintegration-constant of a radio-element.

4·9. Define half-life ($T_{\frac{1}{2}}$) and average life (τ) of a radio-element and obtain mathematical expressions for both of them. Find the relation between $T_{\frac{1}{2}}$ and τ. What are the common units of radioactivity ?

4 10. State and explain Fajan and Soddy's *Group displacement law*. How did it help to accomodate the 13 members of the *thorium series* in the nine [at. no. 82 (Th D. *i.e.* Pb) to at. no. 90 Th] available places in the periodic table. Also explain how the idea of isotopes did originate from the group displacement law.

4·11. Show that, when radioactive equilibrium is established among the members of a radioactive series, the condition

$$\lambda_A N_A = \lambda_B N_B = \lambda_C N_C \,.. \qquad \text{holds good,}$$

where A, B, C... are the radioelements of the series in question. What is the relation between the half-lives and the disintegration constants of the members of such a series ?

4·12. State and explain the differences between chemical reactions and nuclear reactions.

4·13. Explain what is meant by *artificial transmutation of elements,* giving suitable examples. Complete the following artificial transmutations :

$$\begin{aligned}
&{}_{24}Cr^{50}(\alpha, n) && \rightarrow \\
&{}_{4}Be^{9} + {}_{1}H^{1} && \rightarrow \quad + {}_{2}He^{4} \\
&{}_{20}Ca^{40}\ (p, n) && \rightarrow \\
&{}_{3}Li^{6} + {}_{1}H^{2} && \rightarrow \quad {}_{1}H^{1} \\
&{}_{13}Al^{27}\ (n, p) && \rightarrow
\end{aligned}$$

4·14. How was artificial or induced radioactivity discovered ? Give at least two examples of such radio-elements. Discuss the more important uses of these artificial radio-isotopes.

4·15. What is meant by *isotopic labelling* of compounds ? Give specific examples, pointing out the objectives behind such labelling.

What is meant by the *specific activity* of a radioactive material ? What is the unit of specific activity ?

4·16. Explain and illustrate the term *nuclear fission.* What is meant by the term *spallation* ? Distinguish between *fission* and *spallation.* Discuss the principles underlying the production of energy continuously through the fission of U^{235}.

4·17. What are the condition necessary to bring about the *fusion* of two light nuclei, leading to the release of energy ? Why such reactions are also known as *thermonuclear reactions* ?

Explain the difference between nuclear fission and nuclear fusion. Compare the efficiency of these two processes as energy sources. Which one of these two processes is the source of energy of our sun and other stars ?

4·18. Give a brief account of the more important uses of the radio-isotopes in different fields of science and technology.

Objective type :

4·19. Answer by *yes* or *no* :

(a) The number of neutrons in the nucleus of an atom is given by $(A-Z)$, where A is the mass number and Z is the atomic number of the element in question.

(b) The difference between the actual mass of an atomic nucleus and the total mass of its constituent particles is called the *mass defect* of the nucleus.

(c) Two nuclei, having same number of protons but different number of neutrons, are known as *isobars*.

(d) Nuclei with same number of neutrons are called *isotones*.

(e) The binding energy of a nucleus is a measure of its stability.

(f) The binding energy per nucleon rises sharply in the low atomic mass region.

(g) Nuclear fusion is an energy releasing process in the high mass number region.

(h) Fission is an exoergic process in the high mass number region.

(i) Above the mass number 200, the atomic nucleus gets considerably deformed and undergo spontaneous disintegration.

(j) Isotopes with n : p-ratio lower than the stable naturally occuring isotope decay by positron emission.

4·20. Fill up the blanks with appropriate words.

(a) Apart from protons, nuclei of atoms contain —— .

(b) The sub-atomic particles having no charge or mass is called —— .

(c) Isotopes are chemically similar because they have the same number of —— in the nucleus.

(d) The energy required to break up a nucleus to the isolated nucleons is known as the —— of that nucleus.

(e) Nuclear fusion is an exoergic process in the —— mass number region.

(f) The mass-number of an atom is given by the total number of —— and —— present in its nucleus.

(g) The difference between the mass number and the atomic number of an isotope gives the number of —— .

(h) The fundamental particle responsible for keeping the atomic nucleons together in the mucleus is ——.

(i) Elements having a n : p-ratio more than 1 (in the low mass number region) decay by —— emission.

(j) The half-life period of a radio-element is less than its average life period.

4·21. Tick the correct answer :

(a) Isobars are atoms having the same (i) atomic number, (ii) atomic mass, (iii) number of neutrons, (iv) mass number.

(b) A nucleus is stable if it contains the same number of (i) protons and positrons, (ii) protons and electrons, (iii) protons and neutrons, (iv) electrons and neutrons.

(c) The mass of an individual atom of nitrogen is (i) 2.32×10^{-23} g. (ii) 14 g. (iii) 6.023×10^{23} g.

(d) Millikan's oil-drop experiment was done to find (i) velocity of an electron, (ii) mass of an electron, (iii) charge of an electron, (iv) e/m-ratio of an electron.

(e) The decay constant of a radio-element has the dimension of (i) mass, (ii) charge, (iii) $(\text{time})^{-1}$, (iv) velocity.

(f) One Curie means an amount of radioactive material which decays at a rate of (i) 10^6-disintegrations per second (dps), (ii) 10^3 dps (iii) $3{\cdot}7 \times 10^{10}$ dps.

(g) When an atom loses one α-particle it is displaced (i) one place to the right, (ii) two places to the left (iii) two places to the right of its original position in the periodic table.

(h) When an atom of medium mass-number is bombarded by high-energy projectiles, the target nucleus is broken down into several fragments. Such a process is called (i) fission, (ii) fiusion, (iii) spallation.

CHAPTER V : ACID-BASE AND SOME RELATED PHENOMENA.

Essay type :

5·1. Define and illustrate the terms, *acids*, *bases*, *neutralisation* and *hydrolysis*, as they are used in the *Arrhenius concept*. Point out the major defects of the Arrhenius concept of acids and bases.

5 2. (a) "All ammonium salts behave as acids and the amides as bases in liquid ammonia solution". Explain and illustrate the above statement in the light of the *solvent-system concept* of acids and bases. (b) Thionyl chloride acts as an acid in liquid sulphur dioxide medium and sodium nitrite behaves as a base in liquid dinitrogen tetroxide". Justify or refute.

5·3. Describe the salient features of the *Bronsted-Lowry* concept of acids and bases. Explain the hydrolysis of sodium acetate in the light of this theory. What are its limitations ?

5·4. Define *acids, bases and neutralization* in terms of the Lewis concept. In what ways does the Lewis theory of acids and bases differ from the Bronsted-Lowry concept ?

5·5. Name the important methods of determining the pH of as aqueous solution. Describe the principles of the hydrogen-electrode method of pH determination, pointing out the limitations of the method. "The *glass electrode method* is more suitable than the hydrogen electrode method for practical purposes." Do you agree ?

5·6. Deduce expressions for (i) hydrolysis constant, (ii) degree of hydrolysis and (iii) the pH of a solution of a salt of a weak acid and a strong base.

5·7. Find the expressions for the pH of (i) a solution of the salt of a strong acid and a weak base and (ii) a solution of the salt of a weak acid and a weak base.

5·8. What are buffer solutions ? Deduce an equation by which the pH of buffers made up of (i) a weak acid and its salt and (ii) a weak base and its salt can be calculated from the knowledge of the concentrations of the ingredients and the dissociation constants of the acid or the base.

5·9. Name the different types of indicators generally used in titrimetric procedures. Show that the *colour change interval* of an acid-base indicator lies in the range of $pk_{In} \pm 1$, where pk_{In} is the negative logarithm of the indicator constant of the indicator in question.

Short answer type :

5·10. What indicators should be used for (i) the titration of a strong acid with a strong base, (ii) a strong acid and a weak base ? Discuss the basis of your choice. "No indicator is suitable for the detection of the end-point of a titration involving a weak acid and a weak base." Do you agree ? If so, why ?

5·11. Explain the following : (a) BCl_3 can act only as a Lewis acid, where as PCl_3 can act both as a Lewis acid and a Lewis base ; (b) Sulphuric acid is stronger than selenic acid ; (c) H_2S is a weaker acid than H_2Te; (d) H_2SO_4 is stronger than H_2SO_3; (e) the acid strength of hypohalous acids change in the order HOCl>HOBr>HOI; (f) CsOH is a stronger base than NaOH; (g) $Be(OH)_2$ is weaker than $Sr(OH)_2$.

5·12. (a) What is meant by *common-ion effect*? (b) "In the selective precipitation of the Gr. II A and B (of analytical chemistry) metal ions in presence of the ions of the subsequent groups, the presence of dil. HCl is absolutely essential." Justify the statement. (c) "Sufficient NH_4Cl must be added to the solution containing Al^{+3}, Fe^{+3} and Cr^{+3} (along with the ions of the subsequent groups) before the addition of ammonium hydroxide in order to precipitate the hydroxides of Fe^{+3}, Al^{+3} and Cr^{+3} selectively". Explain. (d) If sufficient NH_4Cl is not added to a solution containing Ca^{+2}, Sr^{+2}, Ba^{+2} and Mg^{+2} prior to the addition of NH_4OH and $(NH_4)_2CO_3$, magnesium is precipitated along with the carbonates of Ca^{+2}, Sr^{+2} and Ba^{+2}. Why?

5·13. "In a dilute aqueous solution, the *ionic product of water* is a constant at constant temperature." (a) Explain the above statement. (b) Find out the relation between the ionic product and the ionisation constant of water.

5·14. (a) Define pH of an aqueous solution. (b) Will the pH of two aqueous solutions of O.1N HCl and O.1(N) acetic acid be equal? If not, why? (c) How can the pH of an alkaline solution, say O.1(N) NaOH, can be calculated?

Objective type :

5·15. Answer by **yes** or **no** :

(a) Due to its high charge : radius ratio, the bare proton cannot exist in aqueous solution.

(b) All ammonium salts behave as bases in liquid ammonia solution.

(c) Amides behave as acids in liquid ammonia solution.

(d) The CH_3COO^- ion is a strong base, while the Cl^- ion is a weak base.

(e) The degree of dissociation of acetic acid in aqueous solution is decreased when sodium acetate is added to it.

(f) The degree of dissociation of HCl is decreased by the addition of NaCl.

(g) pH of an alkaline solution is always greater than 7.

(h) pH of a 0.1 (N) HCl is equal to the pH of a 0.1N acetic acid solution.

(i) A solution made up of a weak acid and its salt is called a buffer solution.

(j) The glass-electrode method of pH-determination is better than the hydrogen-electrode method.

(k) An aqueous solution of NH_4Cl has a pH greater than seven.

(l) An aqueous solution of sodium acetate turns phenolphthalein pink.

(m) For the titration of a 0.1 N solution of NH_4OH with a 0.1 N soln. of HCl, methyl orange is a good indicator.

5·16. Fill up the gaps with appropriate words :

(a) — donors are acids and proton acceptors are — .

(b) In an aqueous solution the proton exists as — .

(c) A substance which yields the solvent — is an acid and a substance that generates the solvent anion is a — in that solvent.

(d) The conjugate base of a strong acid is — and the conjugate base of a weak acid is — .

(e) According to the Lewis concept, an acid is an — and a base is an — .

(f) In the titration of 0.1 (N) acetic acid by 0.1 (N) NaOH, — indicator is used.

(g) Solutions possessing reserve capacities for resisting the change of H^+ ions or OH^- ions by the additions of small amounts of acids and bases from outside are known as — .

(h) The Henderson equation, relating the pH of a buffer solution (made up of a weak acid and its salt) with the pK_a of the weak acid used, is — .

(i) At 25°C, the value of ionic product of water is — .

CHAPTER VI : OXIDATION AND REDUCTION PROCESSES.

Essay type :

6·1. Give electronic interpretation of the processes of oxidation and reduction. Show that an oxidation process is always accompanied by reduction and *vice-versa*. What is meant by reduction half-reactions and oxidation half-reactions ? Define and illustrate the terms oxidants and reductants, giving suitable examples.

6·2. Describe fully the method of balancing oxidation reduction reactions (also known as redox reactions) by the ion-electron method. Illustrate your answer with three concrete examples.

6·3. Define equivalent weights of oxidising and reducing agents, giving suitable examples. "The equivalent weight of an oxidising agent or a reducing agent is not an absolute constant, it depends on the exact reaction in which it takes part." Do you agree with this statement ? If so, cite specific examples to support your view.

6·4. Explain the term *redox potential*. Clearly explain the relation between the strength of an oxidising or a reducing agent and its redox potential, using specific examples.

6·5. Define normal or standard potential (E^0) of a system. Discuss the significance of the sign of E^0 of a system. Distinguish *normal* and *formal* potentials of a system. Which one of these two is of more practical utility ?

6·6. Name the factors which affect the E° values of redox systems. Explain the following :

(a) The E° values of the Cu^{+2}/Cu^{+} system and the $\frac{1}{2}I_2/I^-$ system are +0.15 v and +0.535 v respectively. Yet we find that, in dilute aqueous solution, Cu^{+2} oxidises I^- to I_2.

(b) The E° values of the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ system (in neutral solution) and the $\frac{1}{2}I_2/I^-$ system are +0.36 v and +0.535 v respectively. But, we find that, in 1M HCl or H_2SO_4, $[Fe(CN)_6]^{3-}$ oxidises I^- to I_2.

(c) The E° values of the system Co^{+3}/Co^{+2} is 1.82 volts and that of the Ce^{+4}/Ce^{+3} is 1.61 volts. Yet Co^{+2} can be completely converted to Co^{+3} by Ce^{+4} in presence of the complexing agent EDTA.

6·7. "The E° values of different redox-systems can be utilised in (a) predicting the courses of redox reactions involving them and (b) to calculate the equilibrium constants of those redox reactions." Cite specific examples to prove and illustrate the above statements. What is the significance of a high value of K in such redox reactions ?

6·8. Show, by giving concrete examples, that E° values of individual oxidation and reduction reactions (electrode reactions) can be utilised for the calculation of (a) the potentials of the cells obtained by their combination and (b) the equivalence point of redox-titrations involving them.

6·9. What are *redox indicators* ? Illustrate, with a specific example, the choice of a redox indicator for titrating a reductant with an oxidant. Take the example of the titration of Fe^{+2} by $K_2Cr_2O_7$ in acid solution.

6·10. What indicator will you select for determining the end-point of the titration of iodine with thiosulphate ? Is it a redox indicator ? Explain the mechanism of action of such an indicator.

6·11. In an aqueous solution containing Ce^{+4} and Ce^{+3} ions, the value of the redox potential of the system, $Ce^{+4}+e=Ce^{+3}$, is found to be 1.44 volts. If the E° value of the same system is 1.61 volts, calculate the ratio $[Ce^{+4}]/[Ce^{+3}]$ in such an aqueous solution. If some Ce^{+3} ions are added from outside, will the potential increase above 1.44 volts or decrease ? What will be the value of the potential, if the concentration of Ce^{+4} is increased ten-fold ?

Short answer type :

6·12. Complete the following reactions and balance them, keeping in mind that they take place in aqueous acidic medium :

$MnO_2+4Cl^- \rightarrow Mn^{+2}+2Cl^-+Cl_2$

$CuS+NO_3^- \rightarrow Cu^{+2}+SO_4^{2-}+NO$

$HS_2O_3^- \rightarrow S+HSO_4^-$

$MnO_4^{2-} \rightarrow MnO_2+MnO_4^-$

$2MnO_4^-+5SO_3^{2-} \rightarrow 2Mn^{+2}+5SO_4^{2-}$

$I^-+H_2SO_4$ (hot. conc.) $\rightarrow I_2+SO_2$

$Zn+NO_3^- \rightarrow Zn^{+2}+NH_4^+$

$Ag+NO_3^- \rightarrow Ag^++NO$.

6·13. Complete the following reactions and balance them, keeping in mind that the reactions occur in alkaline aqueous solutions :

$N_2H_4+Cu^{+2}+2OH^- \rightarrow N_2+Cu$

$Zn+NO_3^-+OH^- \rightarrow ZnO_2^{2-}+NH_3$

$PbO_2+Cl^- \rightarrow ClO^-+Pb(OH)_3^-$

$ClO^-+Fe(OH)_3 \rightarrow FeO_4^{2-}+Cl^-$

$[Co(CN)_6]^{4-}+O_2 \rightarrow [Co(CN)_6]^{3-}$.

6·14. Consult the table (Table 6·3, p. 268, vol. 1) of redox potentials and select oxidising agents capable of oxidising (a) I^- to I_2 ; (b) Fe^{+2} to Fe^{+3} ; (c) Cl^- to Cl_2 ; (d) Sn^{+2} to Sn^{+4} ; (e) Br^- to Br_2 ; (f) Cu^{+1} to Cu^{+2}.

6·15. In a similar manner, select reducing agents which effect the following reductions : (a) Hg^{+2} to Hg^{+1} ; (b) Fe^{+3} to Fe^{+2} ; (c) I_2 to I^- ; (d) Cl_2 to Cl^-.

6·16. The following standard electrode potentials are given :

$$Fe^{+3}+e = Fe^{+2}, \quad E^\circ=0.78 \text{ v}$$
$$Tl^+ +e = Tl, \quad E^\circ=-0.35 \text{ v}$$

If a cell is now constructed with one half-cell made up of a solution containing 1M Fe^{+3} and 1M Fe^{+2} into which a Pt-wire is dipped, while the other half-cell is made up of a solution of 1M Tl^+ in which a thallium metal rod is immersed, what will be the answers of the following questions :

(a) Which electrode will be the positive terminal ?

(b) What will be the voltage of the cell ?

(c) What is the net cell-reaction due to which electricity is generated.

(d) What is the value of the equilibrium constant of the cell ?

Objective type :

6·17. Answer by yes or no :

(a) Oxidation and reduction can only occur simultaneously and never alone.

(b) The equivalent weight of an oxidant is its formula-weight divided by the number of electrons taken up by one formula-weight of the oxidant.

(c) The equivalent weight of an oxidant or a reductant is always the same.

(d) The potential of the normal hydrogen electrode is taken to be zero.

(e) The sign of the electrode potential is the same as that of the electrostatic charge on the electrode.

(f) Larger the positive value of E° of a system, greater is its power as reducing agent.

(g) The formal potential value of a system is more useful than the corresponding normal potential value.

(h) The effective potential of a system $M^{+n}+e \rightleftharpoons M^{(n-1)}$ is increased if the reduced form is precipitated out of the solution.

(i) Potential of the system, $MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{+2} + 4H_2O$, will decrease with the increase in hydrogen-ion concentration.

6·18. Fill up the blanks with appropriate words :

(a) In a redox reaction the substance which supplies electrons is — and the substance which takes up electrons is — .

(b) In a Daniel cell, the zinc rod is the — electrode and the copper rod is the — electrode.

(c) The electrode potential of a metal/metal-ion electrode is given by the Nernst eqn. which is —.

(d) A system having a higher — potential value will displace a system having a lower — potential value.

(e) For the titration of ferrous iron by potassium dichromate using diphenylamine indicator, the use of — is essential.

(f) Sulphuric acid and not — acid is used in the titration of ferrous iron by potassium permanganate.

6·19. Tick the correct answers :

(a) Iodine is liberated in a solution containing potassium iodide and potassium nitrite by the addition of (i) NaOH, (ii) $Na_2S_2O_3$, (iii) CH_3COOH (or any other acid).

(b) On reaction with H_2S in aqueous solution, iodine produces sulphur. This reaction shows that (i) iodine is a stronger oxidising agent than H_2S, (ii) H_2S is an oxidising agent, (iii) S^{2-} can be reduced to elemental sulphur.

(c) When excess $SnCl_2$ is added to a solution of $HgCl_2$, the major product formed is (i) Hg_2Cl_2, (ii) Sn, (iii) Hg.

CHAPTER VII : COORDINATION COMPOUNDS AND WERNER'S THEORY.

Essay type :

7·1. Distinguish between *double salts* and *complex compounds*. Briefly outline the methods by which the presence of complex ions in solution can be detected.

7·2. Define and illustrate the following terms : Central metal ion, ligand, complex ion, co-ordination number, co-ordination zone, stability constant of a complex, perfect (penetration) and imperfect (associated) complexes.

7·3. Discuss the IUPAC system of naming complex compounds. Give the names of the following complexes :

$[Cu(NH_3)_4]^{+2}$, $[Ag(CNS)_2]^-$, $[PtCl_4]^{2-}$, $[Co(NH_3)_5Cl]^{+2}$, $[Cr(C_2O_4)_3]^{3-}$, $[Co(en)_2Cl_2]Cl$, $[Co(NH_3)_4CO_3]NO_3$, $[Cr(H_2O)_4Cl_2]^+$, $[Cr(H_2O)_3Cl_3]^0$, $[Fe(CN)_6]^{4-}$, $[Fe(CN)_5NO]^{2-}$, $[Pt(NH_3)_2Cl_2]$.

7·4. State the postulates of Werner's theory of co-ordination complexes, citing relevant examples.

7·5. Describe how Werner proved that six co-ordinated complexes possess octahedral stereochemistry.

7·6. Discuss, with examples, the different types of isomerism encountered among co-ordination complexes.

7·7. A compound of molecular formula $CoCl_3.5NH_3$ gave the following reactions :

(i) $CoCl_3.5NH_3 + AgNO_3$ (excess) $\rightarrow CoCl(NO_3)_2.5NH_3 + 2AgCl$

(ii) $CoCl_3.5NH_3 \xrightarrow[\text{at } 110° - 120°C]{\text{heat}}$ No change

(iii) $CoCl_3.5NH_3 + HCl \rightarrow$ No change

(iv) $CoCl_3.5NH_3 \xrightarrow[100°C]{\text{excess KOH soln.}} Co_2O_3 + 3KCl + 5NH_3$

(v) $CoCl_3.5NH_3 \xrightarrow[Ag_2O]{\text{moist}} Co_2O_3 + 5NH_3 + 3AgCl$

(vi) $2CoCl_3.5NH_3 \xrightarrow{\text{conc. } H_2SO_4} Co_2(SO_4)_3 + 5(NH_4)_2SO_4$

(vii) $CoCl_3.5NH_3 \xrightarrow{\text{KI soln.}} CoCl.I_2.5NH_3 + 2KCl$

$$\downarrow AgNO_3$$

$$CoCl(NO_3)_2.5NH_3 + 2AgI.$$

In the light of the above reactions, suggest a plausible structure for the compund $CoCl_3.5NH_3$.

7·8. Briefly discuss the more important applications of complex compounds in different fields.

7·9. What are *chelating ligands* and *metal chelates*. Classify the chelating ligands depending on the number of donor-sites present in one molecule of the ligand, giving at least one example in each case.

7·10. Define and illustrate (with figures) inner metallic complexes of (a) the first order and (b) the second order. Give examples of cationic boron and cationic silicon.

Short answer type :

7·11. Give, with figures, the number of geometrical isomers in each of the following cases :

(a) Square planar complexes of the formulae $[Pt(NH_3)_2Cl_2]$ and $[Pt(NH_3)_3Cl]^+$.

(b) Octahedral complexes of the formulae $[Co(NH_3)_4Cl_2]$, $[Co(NH_3)_3Cl_3]$ and $[Co(en)_2(NO_3)_2]^+$.

(c) Which one of the above octahedral complexes are capable of exhibiting optical isomerism ? Give the structures of the enantiomorphs.

(d) Can $[Co(C_2O_4)_3]^{3-}$ and $[Cr(en)_3]^{+3}$ exist as enantiomers ? If so, give their structures.

7·12. (a) Which of the following ligands can form chelate complexes :

ethylenediamine, water, oxalate ion, glycinate ion, chloride ion, acetylacetone.

(b) Which ones of the above ligands can form inner-metallic complexes of the first order ?

(c) Which ones of the above ligands can form inner-metallic complexes of the 2nd order ?

7·13. Explain the following :

(a) The detection of Cu^{+2} by the addition of excess ammonium hydroxide to an aqueous solution containing Cu^{+2} is based on the formation of a copper complex.

(b) Separation of Cu^{+2} and Cd^{+2} in Gr.IIA of analytical chemistry is based on the difference in stability of the cyano-complexes of Cu^{+2} and Cd^{+2}.

(c) Detection of cobalt by potassium thiocyanate is based on the formation of a thiocyanato complex of cobalt (II).

(d) Estimation of Ni^{+2} (as the dimethyl glyoxime complex) in presence of Fe^{+3} and Cr^{+3} by using tartaric acid is dependent on the relative stabilities of the tartaric acid complexes of Ni^{+2}, Fe^{+3}, and Cr^{+3}.

7·14. Account for the following observations :

(a) $[Co(NH_3)_6]^{+3}$ and $[Fe(CN)_6]^{3-}$ are octahedral.

(b) $Ni(CO)_4$ is tetrahedral.

(c) $[Ni(CN)_4]^{2-}$ is square planar.

(d) $[Ni(NH_3)_6]^{+2}$ is octahedral.

7·15. Give the structure of the possible isomers of the following and write their IUPAC names under each structures :

$CrCl_3.6H_2O$	$[Cr(C_2O_4)_3]^{3-}$
$[Co(NH_3)_4(NO_2)_2]^+$	$[Cr(en)_3]^{+3}$
$[Cr(en)_2Br_2]^+$	
$[Pt(en)Cl_2]$	

Objective type :

7·16. Answer by yes or no :

(a) A double salt, on dissolution in water, gives the tests for all the constituent ions.

(b) When excess NH_4OH is added to a solution of $CuSO_4$ in water, the blue colour of the solution is due to the formation of a double salt.

(c) An abnormal increase in solubility of a sparingly soluble compound due to the addition of a new compound is indicative of complex formation.

(d) $K_2Cd(CN)_4$ is an imperfect complex, but $K_2Cu(CN)_4$ is a perfect complex.

(e) The IUPAC name of $[Co(NH_3)_5H_2O]Cl_3$ is pentammine aquo cobalt (III) chloride.

(f) In $Ni(CO)_4$, the nickel atom is in the sp^3 hybridised state.

(g) The complex $[Cr(en)_2Cl_2]Cl$ can give rise to optical isomers.

(h) $Pt(NH_3)_2Cl_2$ can not give rise to cis-trans isomerism.

(i) Acetylacetone can form inner-metallic complex with Zinc(II) and Co(II).

(j) In the nickel (II) dimethylglyoxime complex, the trans-structure is stabilised by hydrogen bonding.

7·17. Fill up the blanks by appropriate words :

(a) In the complex $Co(NH_3)_6Cl_3$, the ammonia molecules are called —— .

(b) The coordination number of cobalt (III) in the above complex is —— .

(c) The stereochemistry of the above complex is —— .

(d) Ethylenediamine is a —— ligand in the complex $Co(en)_3Cl_3$.

(e) In square planar complexes of the type MA_2B_2, —— isomerism can occur.

(f) —— isomerism is possible in complexes containing an ambidentate donor inside the cordination zone.

7·18. Tick the correct answers :

(a) Optical activity is possible in (i) $[Co(NH_3)_6]^{+3}$, (ii) $[Cr(H_2O)_3Cl_3]^0$, (iii) $[Co(en)_2Cl_2]^+$.

(b) The shape of $[Ni(CN)_4]^{2-}$ is (i) tetrahedral, (ii) square planar, (iii) pyramidal.

(c) The type of hybridisation involved in $[Fe(CN)_6]^{4-}$ is (i) sp^3d^2, (ii) dsp^3, (iii) d^2sp^3.

(d) Among the following complex compounds, the one exhibiting highest conductance value is (i) $[Co(NH_3)_6]Cl_3$ (ii) $Co(NH_3)_4(H_2O)Cl]Cl_2$, (iii) $[Co(C_2O_4)(NH_3)_4]Cl$.

CHAPTER VIII : INERT GASES OR RARE GASES.

Essay-type :

1. Write a short account of the discovery of the inert gases. Why are they so called ?

2. Name the inert gases. What are their sources and how are they isolated ? Discuss their properties and uses.

3. Discuss the position of the inert gases in the Periodic Table and justify their placement.

4. Describe a suitable method for the separation of rare gases from their mixture.

5. What are the various sources of helium ? Describe a method of its isolation from any of these sources. Mention the properties and uses of the gas. Do you know any peculiar property of liquid helium ? Discuss it.

6. Describe the procedure of isolating inert gases from liquid air.

7. Give an account of the various types of compounds that are formed by the rare gases. Write down the stucture of xenon-

platinum hexafluoride. Discuss the nature of chemical bond in xenon fluorides.

8. Discuss the important uses of rare gases in industry, scientific research and in everyday life.

Short answer type :

9. Write short notes on : (a) Clathrate or enclosure compounds of rare gases ; (b) Isolation of helium from natural gases ; (c) Justification of the placement of the inert gases in the zero group of the Periodic Table ; (d) Peculiar properties of liquid helium ; (e) Uses of inert gases in industry ; (f) Electronic structure of the atoms of inert gases and its effect.

10. Why the inert gases do not form diatomic molecules ?

11. Comment on the following : (a) There is very little likelihood of the formation of compounds of He and Ne ; (b) Discovery of the rare gases has completed the Periodic Table.

12. How the elementary nature of the inert gases was established ?

13. Give reasons for the inertness of the rare gases.

14. Why the molecules of the rare gases are considered to be monatomic ?

Objective-type :

15. Fill up the blanks :

(a) The value of C_p/C_v of inert gases is — .

(b) Radon is used for treatment of — .

(c) Neon light is — in colour.

(d) Radon is obtained from — .

(e) The inert gas used for filling airships and balloons is — .

(f) Liquid — is very helpful in producing extremely low temperatures.

(g) The inert gas found in appreciable quantity in atmosphere is — .

16. Decide whether the following are *true* or *false* :

(a) Radon may be isolated by the fractionation of liquid air.

(b) The common electronic configuration of the outermost shell of an atom of an inert gas is $s^2p^6d^{10}$.

(c) The moleculs of inert gases are diatomic.

(d) Helium is used in gas balloons instead of hydrogen because it is lighter than hydrogen.

17. Choose the correct answer in the following :

(a) Rare gases are chemically inert because—

(i) they have stable electronic configuration.
(ii) they are electrically neutral.
(iii) they have high ionisation potential.
(iv) they have low electronegativity.
(v) they are monatomic.

(b) The rare gas obtained during radioactive disintegration is (i) Neon, (ii) Radon, (iii) Krypton, (iv) Xenon, (v) Argon.

(c) The rare gas, having the least ionisation potential is (i) He (ii) Ar, (iii) Rn, (iv) Kr, (v) Ne.

CHATER IX : HYDROGEN, WATER AND HYDROGEN PEROXIDE.

Essay-type :

1. Discuss the position of hydrogen in the Periodic Table.

2. Show, with relevant reactions, that hydrogen can be prepared from water, acids and alkalis. How is the gas manufactured ? State the important uses of the gas.

3. Give an account of the isotopes and allotropes of hydrogen.

4. What is heavy hydrogen ? How is it prepared ? Discuss its important reactions. Compare the properties of heavy hydrogen with ordinary hydrogen.

5. What is 'nascent hydrogen' ? Why is it a more energetic reducing agent than ordinary hydrogen gas ? Give a few examples of the stronger reducing power of nascent hydrogen.

6. Give a short account of *ortho* and *para* hydrogen. Are these forms possible also for other gases ? How does the proportion of the above two forms of hydrogen in a volume of the gas vary with temperature ? How *para* hydrogen can be isolated ?

7. What are hydrides ? Give an account of the different types of hydrides, discussing the nature of the bonds involved in their formation.

8. To what causes the hardness of water is due? How hard water is classified. Describe a method for the removal of different types of hardness in water.

9. What are the disadvantages of hard water? Discuss the various methods used for softening hard water.

10. What is *lather*? Why hard water does not form lather? How the hardness of water is estimated?

11. What are ion-exchange resins? How are they used for softening hard water? Discuss the differences between *the permutit process* and *the ion-exchange process* of softening hard water.

12. Describe a method of determining the gravimetric composition of water. Discuss the structure of H_2O molecule.

13. What is *heavy water*? How is it prepared? Discuss the salient properties of heavy water which are different from ordinary water. What are the uses of heavy water?

14. How is hydrogen peroxide prepared (i) in the laboratory and (ii) on a large scale? Mention its important properties and uses.

15. 'Hydrogen peroxide can act both as an oxidising agent and a reducing agent'. Give some examples (with chemical equations) to prove the above statement. What is the reason for such behaviour of hydrogen peroxide? Discuss the formula and the structure of hydrogen peroxide molecule.

16. Describe a method of preparing hydrogen peroxide in the laboratory. How the dilute solution, obtained during the preparation, is concentrated? What is meant by the '*volume-strength*' of H_2O_2 solution? What is Merck's perhydrol?

Short answer type :

17. Write short notes on : (a) Nascent hydrogen ; (b) Atomic hydrogen ; (c) Ortho and para hydrogen ; (d) Isotopes of hydrogen ; (e) Deuterium and its oxide ; (f) Ionic or saline hydrides ; (g) Covalent hydrides ; (h) Metallic or interstitial hydrides ; (i) Hydrolith ; (j) Occlusion of hydrogen ; (k) Water as a solvent ; (l) Catalytic action of water ; (m) Hard and soft water, (m) Permutit process of softening hard water ; (n) Ion-exchange process of softening hard water ; (o) Soft and de-ionised water ; (p) Heavy water (q) Strength of H_2O_2 solution ; (r) Addition com-

pounds of hyrogen peroxide ; (s) Peroxides, peracids and their salts ; (t) Structure of H_2O and H_2O_2 molecules ; (u) Perhydrates ; (v) Electropositive and electrongative character of hydrogen.

18. Explain why :

(a) Nascent hydrogen is a more powerful reducing agent than ordinary molecular hydrogen.

(b) Very pure zinc reacts sluggishly with dilute HCl or H_2SO_4 to produce hydrogen.

(c) Dilute HNO_3 is not used to prepare hydrogen by its reaction with commercial zinc.

(d) H_2O is a liquid while H_2S is a gas at ordinary temperatures.

(e) Hard water is not used in boilers.

(f) Chemically pure water should not be used for drinking purpose.

(g) Hydrated barium peroxide, and *not* the anhydrous variety, is used for the preparation of H_2O_2 in the laboratory.

(h) A solution of H_2O_2 is generally stored after adding some preservative.

(i) Hydrogen peroxide can act both as an oxidising and a reducing agent

(j) Permanganic acid and perchloric acid are not peroxy acids.

(k) Molecular hydrogen is chemically not very reactive at ordinary temperatures.

19. What happens when the following react ? Give the necessary chemical equations wherever possible and mention the conditions of the reactions :

(a) Ferro-silicon and soda-lime,

(b) Calcium hydride and water,

(c) Potassium iodide and hydrogen peroxide,

(d) Potassium ferrocyanide and hydrogen peroxide,

(e) Potassium ferricyanide and hydrogen peroxide,

(f) Silver oxide and hydrogen peroxide,

(g) MnO_2 (added in small quantity or in excess) and a solution of H_2O_2,

(h) Barium hydroxide and hydrogen peroxide,

(i) Chromic acid ($K_2Cr_2O_7$+dil. H_2SO_4) and hydrogen peroxide.

Objective-type :

20. Decide whether the following are *true* or *false* :

(a) In ortho hydrogen, the nucleii spin in opposite directions.

(b) Hydrogen peroxide molecule is planar.

(c) Heavy water is obtained by exhaustive electrolysis of ordinary water made alkaline.

(d) Ionic hydrides react with water to give basic solutions.

(e) Heavy hydrogen (deuterium) has the same number of nucleons as ordinary hydrogen.

(f) Isotopes of hydrogen have different number of protons.

21. Fill up the blanks :

(a) Ordinary hydrogen is a mixture of ——% ortho H_2 and —% para-H_2.

(b) An example of metallic hydride is —— .

(c) High boiling point of water is due to —— .

(d) When molten salt-like hydrides are electrolysed hydrogen goes to the ——.

(e) In para hydrogen, the two nucleii have —— spins.

(f) The hydride ion is isoelectronic with —— .

(g) SiH_4 is an example of —— hydride.

22. Choose the correct answer :

(a) Heavy water is a compound of—

(i) oxygen and heavier isotope of hydrogen ; (ii) hydrogen and heavier isotope of oxygen ; (iii) heavier isotopes of both hydrogen and oxygen.

(b) Isotopes of hydrogen have—

(i) different number of electrons ; (ii) different number of protons ; (iii) different number of neutrons.

(c) Ionic hydrides react with water—

(i) to give acidic solutions ; (ii) to give basic solutions ; (iii) to produce hydride ions ; (iv) to produce protons ; (v) to produce hydronium ions.

(d) Ortho and para hydrogen—

(i) have different masses ; (ii) have different atomic numbers ; (iii) have nucleii spinning in different ways ; (iv) have electrons spinning in different ways.

(e) High boiling point of water is due to the presence of—

(i) polar bond ; (ii) hydrogen bond ; (iii) electrovalent bond ; (iv) covalent bond.

(f) The sample of hydrogen produced by the electrolysis of dil. H_2SO_4 using Pt-electrodes under high current density is termed

(i) nascent hydrogen : (ii) atomic hyydrogen ; (iii) active hydrogen ; (iv) ortho hydrogen.

(g) When a crystalline substance is exposed to air, it may crumble to a powder. The phenomenon is called

(i) hydration ; (ii) deliquescence ; (iii) efflorescence.

23. Arrange the following hydrides in the decreasing order of their (a) stability, (b) solubility in water and (c) acidity :

(i) NH_3 ; (i) PH_3 ; (iii) AsH_3 ; (iv) SbH_3 and (v) BiH_3.

CHAPTER X : METALS AND METALLURGY.

Essay-type :

1. How do the metals occur in nature ? What is the difference between the *'ore'* and *'mineral'* of a metal ? Discuss the various operations necessary for obtaining a metal in the pure state from one of its ores.

2. What is meant by the term *'metallurgy'* ? Describe briefly the following metallurgical operations : (a) concentration of ore ; (b) calcination and roasting ; (c) reduction and (d) refining of metal.

3. Discuss, with suitable examples, the verious processes of refining crude metals.

Short answer type :

4. Write short notes on :

(a) Ores and minerals ; (b) Gangue, flux and slag ; (c) Calcination and roasting ; (d) Magnetic concentration of ores ; (e) Refining of crude metals ; (f) Zone refining ; (g) Electrostatic concentration of ores ; (h) Self-reduction and air-reduction processes in metallurgy ; (i) Electrolytic reduction process in metallurgy ; (j) Electro-refining of metals ; (k) Thermal refining of metals. (l) Thermit process in metallurgy.

5. Explain why
(a) metals are generally good conductors of electricity ;
(b) electrical resistance of metals increases with temperature ;
(c) metals are generally malleable and ductile ;
(d) metals are generally lustrous and opaque.

Objective-type :

6. Decide whether the following statements are *true or false* :

(a) In air-reduction process, an oxide of a metal is reduced by air.

(b) Calamine ($ZnCO_3$) ore is roasted to transform it into ZnO.

(c) Self-reduction process is employed in the metallurgy of copper and lead.

(d) Highly electropositive metals are generally found *native*.

(e) The metals have higher densities than the non-metals.

CHAPTER XI : ELEMENTS OF THE FIRST GROUP.

Essay-type :

1. Compare the properties of the metals of Group IA (the alkali metals) and those of their principal compounds.

2. Compare and contrast the chemistries of the metals of Groups IA (the alkali metals) and IB (the coinage metals). Discuss the justification of placing the coinage metals in Group I of the Periodic Table.

3. Give the electronic configurations of the alkali metals and discuss some of their important properties in the light of such configurations.

4. How does lithium occur in nature ? Describe a method of isolation of the metal from one of its important ores. Mention the important properties and uses of lithium.

5. Show, with suitable examples, that lithium differs considerably from the other alkali metals. How would you account for such behaviour of lithium ?

6. "Lithium shows much resemblance to another metal belonging to the next higher group of the Periodic Table". What is this phenomenon called ? Cite examples to corroborate the above observation.

7. Describe the manufacture of sodium by the Castner's process. State the important properties and uses of the metal. Give a sketch of the apparatus used.

8. How is sodium manufactured from common salt ? Discuss, with equations, the reactions of the metal with (a) hydrogen, (b) carbon dioxide, (c) ammonia, (d) water and (e) aluminium chloride.

9. Starting from common salt, how would you manufacture five important chemicals ? Mention the important uses of the products you mention.

10. Describe the manufacture of caustic soda by the *amalgam process*, indicating the electrochemical principle involved therein. State the important uses of the material.

11. Describe the method of the manufacture of sodium carbonate by the Solvay process. What is the more valuable ingredient in the process and how is it recovered after the preparation of sodium carbonate ?

12. How is potassium carbonate prepared on a large scale ? Why it cannot be manufactured by the Solvay process ? Discuss the important uses of potassium carbonate.

13. How cesium and rubidium occur in nature ? Describe their extraction and important uses.

14. "The chemistry of the alkali metals may be regarded as the chemistry of their ions."—Discuss.

Short answer type :

15. Write short notes on : (a) Causticisation of sodium carbonate ; (b) Salt cake ; (c) Soda ash ; (d) Pearl ash ; (e) Leblanc process of the manufacture of sodium carbonate.

16. How the following substances are prepared and what are their important uses :

(a) Lithium aluminium hydride ; (b) Sodium peroxide ; (c) Sodamide ; (d) Sodium nitrite ; (e) Sodium sulphide ; (f) Sodium bicarbonate ; (g) Potassium bromide ; (h) Potassium cyanide ; (i) Potassium bisulphate.

17. Explain why

(a) The alkali metals do not occur in nature in the free state.

(b) Metallic sodium cannot be prepared through the electrolysis of an aqueous solution of NaOH or NaCl.

(c) Lithium exhibits much resemblance to magnesium.

(d) Lithium carbonate decomposes on heating to give CO_2, but carbonates of the other alkali metals do not.

(e) Potassium carbonate cannot be manufactured by the Solvay process.

(f) Potassium hydroxide solution, and not sodium hydroxide solution, is used to absorb CO_2 in the estimation of carbon.

(g) Ionisation potential values of alkali metals are comparatively high.

18. What happens when :

(a) Caustic soda reacts with (i) chlorine, (ii) aluminium and (iii) arsenious sulphide ?

(b) Sodium nitrate reacts with caustic soda and zinc dust ?

(c) Sodium carbonate solution is added to a solution of ferric chloride ?

(d) Carbon dioxide gas is passed through brine which is saturated with ammonia ?

(e) Lithium carbonate and sodium carbonate are separately heated ?

(f) Ammonia gas is passed over a mixture of carbon and molten potassium carbonate ?

Mention the conditions of the reactions and write down their equations.

19. Distinguish between diaphragm cell and mercury cathode cell as used in the manufacture of caustic soda by electrolytic process.

Objective-type :

20. Fill up the blanks :

(a) —— is the lightest of all the metals.

(b) Lithium can be obtained by the electrolysis of a fused mixture of —— .

(c) Lithium burns in nitrogen to form —— .

(d) Sodium is —— electropositive than potassium.

(e) Lithium aluminium hydride is obtained by treating an excess of —— with an ethereal solution of $AlCl_3$.

(f) The alkali metal, required as a nutrient for plant-growth is —— .

(g) The oxidation number of sodium in Na_2O_2 is —— .

21. Decide whether the following are *true* or *false* :

(a) Sodium amalgam is used as a reducing agent.

(b) An alloy of sodium and potassium is a liquid.

(c) Sodium peroxide liberates H_2O_2 on treatment with warm dilute acids.

(d) Lithium resembles magnesium, since their electronegativities are almost the same.

(e) The electronegativity increases from Li to Cs.

(f) Like sodium chloride, lithium chloride is also soluble in water.

(g) Like potassium carbonate, lithium carbonate is also freely soluble in water.

22. Pick up the correct answer in the following :

(a) From the trends observed in the group of the alkali metals, francium should be

(i) more electropositive than cesium.
(ii) the lightest of these elements.
(iii) biggest in the size of its atom.
(iv) the least ionisable.

23. Pick out the correct statements—

(a) The electronegativities of all the alkali metals are the same.

(b) Lithium resembles magnesium in some respects though placed in different groups of the Periodic Table.

(c) The electropositive character of the alkali metals decrcases with the increase of atomic number.

(d) Alkali metals are strong reducing agents.

(e) Sodium and potassium may be characterised by their line spectra.

(f) The flame coloration due to the alkali metals is due to their low boiling points.

(g) The alkali metals readily dissolve in liquid ammonia to give blue solution which is believed to be due to

(i) ammoniated cations ;
(ii) ammoniated anions ;

(iii) ammoniated electrons ;
(iv) ammoniated cations and ammoniated electrons ;
(v) ammoniated anions and ammoniated electrons,

(h) Sodamide is prepared by
(i) heating soda ash in ammonia
(ii) passing nitrogen over molten sodium
(iii) passing ammonia gas over molten sodium
(iv) passing ammonia gas through molten sodium chloride
(v) passing ammonia gas through molten sodium hydroxide.

24. Which of the following commercial names in the first column correspond to the chemical formulae in the second column :

(a) Soda ash	$NaOH$
(b) Glauber's salt	$NaNO_3$
(c) Saltpetre	Li_2O
(d) Baking soda	Na_2CO_3
(e) Lithia	K_2CO_3
(f) Pearl ash	$NaHCO_3$
	$Na_2SO_4.10H_2O$
	$Na_2CO_3.10H_2O$
	Na_2SO_4.

CHAPTER XII : THE COINAGE METALS.

Essay-type :

1. What are the coinage metals ? Why are they so called ? Compare the characteristics of the coinage metals and their important compounds. How far it is justified to place them in Group I of the Periodic Table ?

2. Write down the electronic configurations of the atoms of the coinage metals and discuss the important characteristics of these metals that are the outcome of such configuration. Why the bivalent copper salts are more stable than the monovalent copper salts ?

3. Give the names and the chemical compositions of the important ores of copper. How is the pure metal obtained from its sulphide ore ? Name some important alloys of copper and mention the uses of the metal and its important alloys.

4. How is copper obtained from its ores by the *wet process* ? Starting from metallic copper, how would you prepare the following compounds : (a) cupric chloride, (b) cuprous chloride, (c) cuprous iodide, (d) cuprous thiocyanate and (e) cuprous cyanide ?

5 How is copper sulphate manufactured ? Mention its important uses. How copper sulphate reacts with the following (mention the conditions of the reactions and give the chemical equations) :

(a) ammonium hydroxide solution, (b) potassium iodide solution, (c) potassium thiocyante solution, in presence of SO_2, (d) metallic copper, (e) phosphorus, (f) caustic soda solution in the cold and when heated.

6. What are the chief ores of silver ? Name some principal processes for the extraction of silver from its ores, discussing the chemistry involved in each of them.

7. What do you understand by the term "*desilverisation of lead*" ? Deseribe an important method of isolating silver from a lead ore. How is the metal purified ? State the uses of silver.

8. Give an account of the higher-valent compounds of silver.

9. Discuss the use of silver halides in photography and the chemistry involved in it.

10. How does gold occur in nature ? Describe the important methods used for the extraction of gold from its natural sources, mentioning the chemistry involved in them. How is gold (III) chloride prepared and what are its uses ?

Short answer type :

11. Write short notes on :

(a) Blister copper, (b) Schweitzer's reagent, (b) Desilverisation of lead, (d) Cupellation, (e) Spitting of silver. (f) Quartation, (g) Use of silver halides in photography, (h) Purple of Cassius, (i) Fulminating gold.

12. (a) How are the following substances prepared :

(i) cuprous chloride, (ii) cuprous cyanide, (iii) silver nitrate, (iv) chloroauric acid.

Mention their important uses.

(b) Discuss the use of silver nitrate in chemical analysis.

13. What happens when :

(a) Silver chloride is
- (i) boiled with a solution of caustic soda,
- (ii) treated with a solution of ammonia,
- (iii) fused with sodium carbonate,
- (iv) treated with nascent hydrogen,
- (v) treated with potassium cyanide solution,
- (vi) treated with sodium thiosulphate solution:

(b) A solution of silver nitrate is treated with
- (i) a solution of potassium cyanide
- (ii) a solution of sodium thiosulphate
- (iii) a solution of potassium thiocyanate
- (iv) a solution of ammonia
- (v) a solution of sodium chloride, followed by a solution of ammonia.

(c) A solution of copper sulphate is treated with
- (i) a solution of ammonia,
- (ii) a solution of sodium carbonate,
- (iii) a solution of sodium cyanide,
- (iv) a solution of potassium ferrocyanide.

(d) Dilute sulphuric acid is added to cuprous oxide and cupric oxide separately.

(e) Dilute nitric acid is added to cuprous oxide and cupric oxide separately. Give chemical equation in each case.

14. Explain why

(a) The coinage metals are much less reactive than the alkali metals, although an atom of both contains a single electron in its outermost shell.

(b) The monovalent compounds of copper are generally colourless (or white), while the bivalent compounds are generally coloured.

(c) Iodine is liberated when KI is added to a solution of Cu^{++} ions, but chlorine is not liberated when KCl is added.

(d) Alkali metals are always monovalent, while coinage metals show variable valency, although both contain a single electron in their outermost electronic shells.

(e) Simple compounds of bivalent gold are not available.

(f) Cuprous and aurous compounds are unstable and Ag (II) compounds are not common.

(g) The coinage metals often form covalent simple compounds.

Objective-type :

15. Complete the following :

(a) The chemical name of *Lunar caustic* is —— .

(b) The size of the gold atom is almost the same as that of the silver atom due to —— .

(c) The increased density of the coinage metals is due to —— .

(d) Coinage metals (and their ions) are of smaller size than those of alkali metals due to —— .

(e) Copper does not dissolve in dilute H_2SO_4 with the evolution of hydrogen due to —— .

(f) German silver is an alloy containing —— .

16. Fill up the blanks :

(a) Among the coinage metals, — has the biggest size.

(b) Gold dissolves in — and the main product is —.

(c) Proustite is an ore of —.

(d) Sodium thiosulphate is used as a — agent in photography.

(e) In India, gold is available at —.

(f) Silver chloride dissolves in ammonia solution with the formation of —.

17. Pick up the correct answer :

(a) A photographic plate is usually coated with a thin film of (i) AgCl ; (ii) AgBr ; (iii) AgI ; (iv) $Ag_2S_2O_3$; (v) AgOH.

(b) 'Lunar Caustic' is the name of—

(i) Ag_2O ; (ii) AgO ; (iii) AgOH ; (iv) $AgNO_3$; (v) Ag_2SO_4 ; (vi) $[Ag(NH_3)_2]OH$.

(c) Skin is stained black in contact with silver nitrate due to

(i) the incipient charring of skin,

(ii) the deposition of black silver sulphide,

(iii) the deposition of Ag_2O,

(iv) the deposition of finely divided silver.

(d) A boiled egg tarnishes a silver spoon black. It is due to

(i) the formation of finely divided Ag,

(ii) the formation of Ag_2O,

(iii) the formation of AgCl which darkens on exposure to light,

(iv) the formation of silver sulphide.

(e) Match the names of the metals in the first column with the names of the ores in the second column :

Copper	Proustite
Silver	Calaverite
Gold	Chalcocite
	Anglisite
	Brucite
	Smaltite.

CHAPTER XIII : ELEMENTS OF GROUP II.

Essay-type :

1. Mention the general electronic configuration of the metals of Group IIA and that of the metals of Group IIB and discuss the important characteristics of the metals of the two sub-groups.

2. Compare and contrast the chemistry of the metals of Group IIA with that of the metals of Group IIB.

3. Discuss the analogies between magnesium, calcium, strontium and barium on the one hand, and zinc, cadmium and mercury on the other hand, and hence, justify the position of magnesium as a bridge element between the two sub-groups.

4. Discuss, with suitable examples, the speciality in the chemistry of mercury, as compared with the other metals of Group II.

5. Name and give the chemical composition of the most important mineral of beryllium. How is the metal extracted from it ? State the uses of the metal and some of its important alloys.

6. Compare the properties of beryllium with those of the other metals of Group II, and discuss the statement that 'beryllium resembles more or less closely aluminium, a member of the next higher group of the Periodic Table'.

7. What are the '*alkaline earth metals*' ? Why are they so called ? Write a short account of their isolation and uses. Starting

with their sulphate, how would you prepare (a) one of the metals, (b) one of their peroxides and (c) one of their soluble salts.

8. What are the chief ores of magnesium ? How is the metal extracted ? Discuss the chemical relationship of magnesium with calcium and zinc.

9. How is metallic magnesium obtained from sea-water ? Why has the metal become one of the important metals used in industry ? State the name, composition and uses of some of its important alloys. What is 'magnesia mixture' and what is its reaction with a solution of an arsenate ?

10. What is bleaching powder ? How is it prepared ? State its important properties and uses. Discuss the constitution of bleaching powder. How could you estimate the amount of *available chlorine* in a sample of bleaching powder ?

11. How is calcium carbide obtained on a commercial scale ? What are its important properties and uses ? How calcium carbide can be converted into calcium cyanamide ? Give the important uses of calcium cyanamide.

12. How does barium occur in nature ? How is the metal prepared from its important source ? Describe the preparation and mention the uses of the following :

(a) Barium peroxide, (b) Barium chloride, (c) Barium carbonate, (d) Lithopone.

13. Name, with chemical composition, two important ores of strontium and describe the isolation of the metal from them. Mention some important compounds of the metal and describe their preparation.

14. Describe the preparation of radium from its important natural source. State the characteristic properties and uses of the metal.

15. Give the names and formulae of the important ores of zinc. What principles are involved in the extraction of metallic zinc from its ores ? Describe a continuous process of the metallurgy of the metal. Why cannot magnesium be prepared in a similar manner ?

16. What is the main source of metallic cadmium and how is it obtained therefrom ? Name the important alloys of cadmium

and mention their uses. Discuss the nature of cadmium iodide in aqueous solution.

17. How does mercury occur in nature ? Describe how the metal is obtained from its important ore and purified. What are the characteristic uses of the metal and on what do they depend ? Describe the prepartion of the halides, nitrates and sulphates of mercury.

18. How is commercial mercury purified ? Describe the action of heat on the following mercuric salts : chloride, cyanide, nitrate, nitrite, sulphide and thiocyanate. Give equation in each case. Describe two simple tests by which you could distinguish mercurous chloride from mercuric chloride.

19. What is Nessler's reagent ? How is it prepared ? Mention its use, indicating the reactions involved.

20. Give a short account of ammonia-mercury compounds.

21. "Mercury is formally bivalent, although electrochemically unipositive in the mercurous compounds." —Mention the various experimental proofs to corroborate the above statement.

22. Compare the properties of the metals of Group IIB and their important compounds.

23. Starting from metallic mercury, how would you prepare the following : (a) mercurous nitrate, (b) mercuric oxide, (c) mercurous chloride and (d) mercuric chloride. Mention the important uses of these compounds.

Short answer type :

24. Write short notes on :

(a) Carbothermal process of extraction of magnesium, (b) Sorel's cement, (c) Quick lime and slaked lime, (d) Anhydrone, (e) Epsom salt, (f) Bleaching powder, (g) Plaster of Paris, (h) Calcium carbide, (i) Superphosphate of lime, (j) Lithopone, (k) Spelter, (l) Philosopher's wool, (m) Galvanising and sherardizing of articles, (n) Rinmann's green, (o) Separation of Cu^{++} and Cd^{++} in qualitative analysis, (p) Calomel, (q) Corrosive sublimate, (r) Fusible and infusible white precipitates, (s) Millon's base, (t) Nessler's reagent.

25. How are the following substances prepared ? What are their important uses ?

(a) Anhydrous magnesium chloride, (b) Magnesium perchlorate, (c) Magnesium sulphate heptahydrate, (d) Magnesium carbonate, (e) Calcium hydride, (f) Quicklime, (g) Fused calcium chloride, (h) Bleaching powder, (i) Plaster of Paris, (j) Calcium carbide, (k) Calcium cyanamide, (l) Barium peroxide, (m) Lithopone, (n) Anhydrous zinc chloride, (o) Calomel, (p) Corrosive sublimate.

26. Explain why

(a) Beryllium shows covalency, while the other members of the alkaline earth family show electrovalency.

(b) NaOH is a stronger base than $Ba(OH)_2$.

(c) The 1st ionisation potentials of the alkaline earth metals are very low as compared with the 2nd ionisation potentials.

(d) Beryllium differs much from the rest of the alkaline earth metals.

(e) Although Zn and Ca both have $4s^2$ electrons in their valency shells, yet they differ considerably from each other.

(f) The alkaline earth metals are harder, denser and melt at higher temperatures than the alkali metals.

(g) $Mg(OH)_2$ is not precipitated by NH_4OH from solutions containing large excess of NH_4Cl.

(h) Anhydrous magnesium chloride cannot be prepared by heating $MgCl_2.6H_2O$.

27. What happens when : (Give conditions and equations of the reactions) :

(a) Water acts separately on (i) metallic calcium, (ii) calcium carbide, (iii) calcium phosphide, (iv) calcium nitride, (v) fused calcium chloride, (vi) calcium cyanamide, (vii) plaster of Paris.

(b) Ammonium hydroxide is added to a solution of zinc chloride (i) in the presence and (ii) in the absence of ammonium chloride. (Give reasons for your answer.)

(c) H_2S gas is passed through a solution of zinc chloride (i) in the presence and (ii) in the absence of NH_4Cl and NH_4OH.

(d) A dilute solution of NH_4OH is added to a solution of Nessler's reagent.

(e) A solution of potassium iodide is added to a solution of mercuric chloride.

(f) Mercuric sulphate and mercuric cyanide are separately heated.

(g) Bleaching powder reacts with a strong aqueous solution of ammonia.

(h) Excess of KCN solution is added to a solution of cadmium chloride and H_2S gas is then passed through the mixture.

(i) Mercurous chloride is treated with ammonia.

(j) A solution of mercuric nitrate is gradually heated.

28. (a) Mention the different tests you would perform to differentiate between a mercuric salt and a mercurous salt.

Objective-type :

29. Complete the following :

(a) Superphosphate of lime is a mixture of—

(b) The formula of beryl is—

(c) Nessler's reagent is — .

(d) Mercury fulminate is — .

(e) The chemical formula of the Millon's base is — .

30. Choose the correct statement in the following :

(a) (i) Beryllium is more electropositive than magnesium.

(ii) Alkaline earth metals are good reducing agents.

(iii) Beryllium resembles aluminium closely in its properties, though it belongs to a different group of the Periodic Table.

(iv) Electronegativities of the alkaline earth metals increase with atomic numbers.

(b) AgCl is soluble in ammonia due to the formation of

(i) $[Ag(NH_3)_2]^{++}$, (ii) $[Ag(NH_3)_2]^+$, (iii) $[Ag(NH_3)_4]^+$, (iv) $[Ag(NH_4)_2]^+$, (v) $AgNH_2$.

(c) Beryllium and aluminium have similar properties because

(i) they belong to the same group of the Periodic Table.

(ii) they have nearly the same electronegativity values.

(iii) they have the same ionisation potential.

(d) Plaster of Paris is

(i) $CaSO_4.H_2O$, (ii) $CaSO_4.2H_2O$, (iii) $CaSO_4.6H_2O$, (iv) $CaSO_4.1{\cdot}5H_2O$, (v) $2CaSO_4.H_2O$.

31. Match the name of the metals in the 1st column with the name of the ores in the 2nd column :

Beryllium	Calamine
Magnesium	Phenacite
Calcium	Witherite
Strontium	Franklinite
	cinnabar
Barium	Greenockite
Zinc	Tiemannite
Cadmium	Celestine
Mercury	Kiesserite
	Phosphorite

CHAPTER XIV : ELEMENTS OF GROUP III.

Essay-type :

1. Give the electronic configurations of boron and aluminium. Compare and contrast the properties of boron with those of aluminium and also those of the compounds of the two elements.

2. What is meant by 'diagonal relationship' in periodic classification ? Discuss the diagonal relationship of boron and silicon.

3. How does boron occur in nature ? Describe the isolation of boron from its important natural source and discuss the important properties and uses of the element.

4. What are the allotropic modifications of boron ? How are they prepared ? Mention the important difference in properties of the allotropes of boron. Starting from a mineral of boron, how would you prepare (a) boric acid, (b) borax and (c) potassium borofluoride ?

5. Give an account of the hydrides of boron with special reference to diborane. Discuss the important properties of diborane.

6. What is diborane ? How is it prepared ? Discuss the structure of diborane.

7. What is borax ? Write down its chemical formula. What are the important natural sources of borax ? Describe the preparation of borax from one of its chief minerals. Starting with borax, how can you obtain (a) boron nitride, (b) boron trioxide, (c) boron trichloride and (d) boric acid ?

8. What is *borax bead test* ? Name the metal ions that can be detected by this test. Discuss the chemistry of borax bead test.

9. Discuss the chemical properties of boron in relation to carbon and aluminium.

10. Give the preparation and properties of the boron halides. Why are tnese halides called *Lewis acids* ?

11. Give a short account of the various boric acids and their salts. How is H_3BO_3 prepared from *colemanite* ? Discuss its important properties and uses.

12. Name the chief ores of aluminium and write down their formulae. How is the metal extracted from its principal ore ? Name some important alloys of aluminium and mention the uses of the metal and its important alloys.

13. How is aluminium extracted from bauxite ? What is the function of cryolite in the above extraction ? Describe the method of refining aluminium.

14. Describe the extraction of aluminium from its silicate ores and clays. In what form and in which localities in India do the aluminium ores occur ?

15. What are alums ? Mention the names and composition of some important alums, How is common alum manufactured and what are its important uses ?

16. Compare boron with silicon.

Short answer type :

17. Write short notes on :

(a) Boron hydrides, (b) Inorganic benzene or borazole, (c) Borax, (d) Borax bead test, (e) Peroxyborates and borate peroxyhydrates, (f) Cationic complexes of boron, (g) Goldschmidt's thermit process, (h) Alumina, (i) Alums, (j) Ultramarine, (k) Complexes of aluminium, (l) Metal borohydrides, (m) Boron nitride, (n) Cryolite.

18. How are the following substances best prepared and what are their uses :

(a) Boric acid, (b) Borax, (c) Anhydrous aluminium chloride, (d) Aluminium sulphate, (e) Potash alum, (f) Ultramarine blue, (g) Synthetic cryolite.

19. Explain why

(a) Boron differs much from aluminium.

(b) While aluminium forms both covalent and electrovalent compounds boron mostly forms covalent compounds.

(c) $B(OH)_3$ is acidic but $Al(OH)_3$ is amphoteric.

(d) Boron halides act as Lewis acid.

(e) Aluminium cannot be prepared by the carbon-reduction of purified alumina.

(f) An aqueous solution of borax is highly alkaline.

(g) An aqueous solution of aluminium chloride reacts acidic.

(h) $AlCl_3$ is low boiling (b.p. 183°C) while AlF_3 is high boiling (b.p. 800°C).

(i) Boric acid is very weak, but it can act as a strong acid on adding glycerol to it.

(j) Boron trifluoride is an acceptor of electron-pair.

20. What happens when (Give the conditions and chemical equations of the reactions) :

(a) A piece of metallic aluminium is dipped in a solution of copper sulphate.

(b) Metallic aluminium is heated in a current of nitrogen.

(c) Metallic aluminium is treated with nitric acid.

(d) A solution of sodium carbonate is added to a solution of an aluminium salt.

(e) Powdered aluminium reacts with Cr_2O_3.

(f) Powdered borax is gradually heated to a high temperature.

(g) Diborane reacts with KOH solution.

(h) Diborane reacts with ammonia.

(i) Boric acid is gradually heated to a high temperature.

(j) Dry ammonia gas is passed over anhydrous $AlCl_3$.

21. How would you prove that (i) aluminium has a great affinity for oxygen ; (ii) BF_3 is an electron-deficient compound, (iii) $Al(OH)_3$ is amphoteric, but $B(OH)_3$ is acidic.

Objective type :

22. Pick up the correct answer :

When orthoboric acid is heated to red heat, the residue is (i) boron, (ii) boron trioxide, (iii) pyroboric acid, (iv) borax, (v) metaboric acid.

23. Which of the following statement regarding H_3BO_3 is false :

(a) It acts as a monobasic acid.
(b) It is formed in the hydrolysis of borax.
(c) It is soluble in hot water.
(d) It has a planar structure.
(e) It acts as a tribasic acid.

24. Choose the correct answer :

(a) Pure boron is best prepared by
   (i) heating B_2O_3 with H_2.
   (ii) heating B_2O_3 with Na or K.
   (iii) heating KBF_4 with Na or K.
   (iv) heating BBr_3 with hydrogen in presence of a catalyst.
   (v) heating KBF_4 with hydrogen in presence of a catalyst.

(b) Inorganic benzene is
(i) B_2H_6, (ii) $B_3O_3H_6$, (iii) BO_3H_3, (iv) $B_3N_3H_6$, (v) BH_3
(c) Barox bead test can be used to detect the presence of
(i) Al, (ii) Mg, (iii) Mn, (iv) Na, (v) Ca.

(d) $B(OH)_3$ is
(i) basic, (ii) amphoteric, (iii) acidic, (iv) neutral, (v) unstable.
(e) B_2O_3 is
(i) acidic, (ii) basic, (iii) ionic, (iv) an ozonide, (v) amphoteric.
(f) BF_3 reacts with NH_3 to form
(i) BN, (ii) $B(NH_2)_3$, (iii) BNH_2F_2+HF, (iv) BF_2NH_3.

25. Complete the following :

(a) — hybridisation is involved in the formation of BF_3.
(q) Aluminium carbonate is not formed due to the fact that — .
(c) BF_3 acts as a strong Lewis acid due to the fact that — .
(d) A solution of borax reacts alkaline due to — .
(e) Crystalline boron is — reactive than amorphous boron.
(f) The formula for *jeweller's borax* is — .
(g) BF_3 is hydrolysed by water to produce — and — .
(h) AlN reacts with heated NaOH solution under pressure to form — and — .
(i) The formula of potash alum is — .

CHAPTER XV: ELEMENTS OF GROUP IV B.

Essay-type :

1. Discuss the chief analogies which justify the inclusion of carbon, silicon, tin and lead in the same group.

2. Compare carbon and silicon, discussing the element and their oxides and chlorides. Compare carbonic and silicic acid and their salts.

3. Compare the physical and chemical propertics of the elements —carbon, sillcon, tin and lead, with special reference to their oxides, hydrides and halides.

4. What are *allotropic modifications* ? How many allotropic modifications of carbon are known ? Discuss them with special reference to their structures, properties and uses. How would you prove that all of them contain one and the same element ?

5. Compare the elements boron; carbon and silicon, along with their important compounds.

6. How the crystalline allotropes of carbon have been obtained artificially. Compare the properties of the various allotropic modifications (both crystalline and amorphous) of carbon.

7. Write a short account of carbides, classifying them according to their structures and also on their behaviour with water.

8. How would you prepare and collect a sample of carbon monoxide ? Write down what you know about the composition and structure of the compound. How and under what conditions does carbon monoxide react with (i) nickel, (ii) cuprous chloride, (iii) sodium hydroxide and (iv) hydrogen ?

9. What are *metal carbonyles* ? Write a short essay on then, indicating their general methods of preparation, properties and structures.

10. Explain what is meant by *crabonisation of coal.* Discuss the relative advantages and disadvantages of the low and high temperature carbonisation of coal.

Describe the high temperature carbonisation of coal, indicating the steps adopted to recover the important by-products.

11. What is *coal gas* ? Write down its average composition. Describe the manufacture of coal gas, mentioning the important by-products of the process and their uses.

12. What are *water gas* and *producer gas*? Describe their manufacture. How can pure hydrogen be obtained from water gas? Mention the uses of the gases.

13. Describe the preparation of carbon disulphide. Discuss its properties and structure. Compare and contract its properties with those of carbon dioxide.

14. Write a short essay on gaseous fuels.

15. Starting from a reasonably pure specimen of natural silica, such as white sand, how would you prepare (i) silicon tetrachloride, (ii) hydrofluosilicic acid, (iii) silica gel (iv) silicon and (c) carborundum.

16. What is glass and how is it made? How glass is classified according to its composition. Discuss the variation of properties of different types of glass. What are coloured glasses? How various colours are incorporated in glass?

17. How the silicates are classified according to their structures? Give an important example of each class of silicate. What are aluminosilicates? Mention some important examples of them.

18. Discuss the structure of SiO_4^{4-}-ion. Show how the different types of silicates structurally arise as a result of different manners in which these structural units of SiO_4^{4-}-ions are linked together.

19. What are silicones and how they are prepared? Discuss the important properties and uses of silicones.

20. How does crystalline silica occur in nature? What different modifications of these forms are known? Discuss the structure of crystalline silica and mention its important properties and uses.

21. What are *silanes* and how they are prepared? Discuss the important properties of the silanes.

22. Name the chief natural source of tin and describe briefly the metallurgy of tin from this source. How and under what conditions does tin react with (i) hydrochloric acid, (ii) nitric acid, and (iii) chlorine? Give equations of the reactions. Name the important alloys of tin and their uses.

23. Compare and contrast the properties of tin and lead, and their chief compounds. Starting from metallic tin, how would you

prepare (i) stannous chloride and (ii) stannic chloride ? Discuss in short, the main characteristics of these two compounds.

Compare the merits and demerits of *tinning* and *galvonisation.*

24. Mention the principal ores of lead and give their formulae. Describe the metallurgy of lead from its principal ore. What valuable metals are generally associated with lead in its ores ? State the important uses of the metal and its important alloys.

25. Describe the concentration of poor argentiferous lead by (i) Pattinson's process and (ii) Parke's process, indicating the theoretical principles involved therein. How do the compounds of quadrivalent lead differ from the corresponding compounds of bivalent lead. Discuss the justification of placing lead in Group IV of the Periodic classification.

26. What is white lead ? Describe the Dutch process of its manufacture. Mention its uses, indicating disadvantages, if any.

27. Describe a lead storage battery and discuss the chemical changes that take place during its charging and discharging.

28. Starting from metallic lead, describe the preparation of the different oxides of lead. What tests would you perform to distinguish between these oxides ?

Short questions :

29. Write short notes on :

(a) Semi-weter gas and carburetted water gas, (b) The usefulness of CO_2 in the life proeesses of plants and animals, (c) Artificial diamond, (d) Artificial graphite, (e) Activated charcoal, (f) Metal carbonyls, (g) Percarbonates and carbonate perhydrates, (h) Phosgene, (i) Freons, (j) Metallic cyanides, (k) Cyanogen, (l) Gaseous fuels, (m) Carbonisation of coal, (n) Silanes, (o) Silico-chloroform, (p) Silicones, (q) Silica gel, (r) Water glass, (s) Cationic silicon, (t) Glass, (u) Annealing of glasswares, (v) Artificial gems (w) Mosaic gold, (x) Carborundum, (y) Calcium carbide, (z) Desilverisation of lead.

30. How are the following substances best prepared :

(a) Activated charcoal, (b) Potassium perdicarbonate, (c) Carbon disulphide, (d) Carbon terachloride, (e) Silicon tetrachloride, (g) Silico-chloroform, (h) Hydrofluosilicic acid, (i) Water glass,

(j) Silica gel, (k) Stannic chloride, (l) Red lead, (m) Lead tetrachloride, (n) Lead tetraacetate ?

31. Explain why

(a) Diamond is very hard while graphite is soft and slippery, although both are the allotropes of carbon.

(b) Graphite conducts electricity but diamond does not.

(c) Carbon dioxide is a gas, while silicon dioxide is a solid.

(d) CO_2 exists as discrete molecules, but SiO_2 forms giant molecules of limitless SiO_2 units.

(e) $SiCl_4$ is hydrolysed by water, but CCl_4 is not.

(f) Lead pipes are not safe for the transport of drinking water.

(g) Lead pipes are slowly corroded by hydrochloric or sulphuric acids but are more rapidly corroded by acetic acid or nitric acid.

(h) Damaged kerosine tins deteriorate quickly.

(i) Lead tetrachloride is known, but not lead tetrabromide or tetraiodide.

(j) The Pb (II) and Sn (II) compounds are more ionic than the Pb (IV) and Sn (IV) compounds.

(k) Wood charcoal (density=1·4—1·9) floats on water.

(l) 10 ml. of N/10 Na_2CO_3 is titrated with a N/10 solution of HCl using phenolphthalein and methyl orange indicators separately. In the first case, the addition of 5 ml. of the acid solution changes the colour of the indicator, while in the second case, 10 ml. of the acid solution are required.

32. What happens when : (Give conditions and equations of the reactions) :

(a) Conc. H_2SO_4 reacts with potassium ferrocyanide.

(b) Carbon monoxide reacts with caustic soda.

(c) Iron pentacarbonyl is dissolved in caustic soda and the solution is then acidified.

(d) A saturated solution of potassium carbonate is electrolysed with Pt electrodes.

(e) Carbon disulphide reacts separately with caustic soda and sodium sulphide.

(f) Fuming H_2SO_4 is added dropwise to boiling carbon disulphide.

(g) A mixture of powdered copper sulphate and potassium cyanide is heated.

(h) Potassium cyanide reacts with red lead.

(i) Silico-methane reacts with an alkali solution.

(j) Silicon tetrachloride is heated with water.

(k) Metallic tin reacts with conc. HNO_3.

(l) A solution of caustic soda reacts with stannous oxide.

(m) A alkaline stannite solution is added to a bismuth salt.

(n) Stannous chloride reacts with iodine.

(o) Lead sulphate is treated with a solution of ammonium acetate.

(p) Red lead is boiled separately with conc. HCl and conc. H_2SO_4.

(q) Red lead is dissolved in glacial acetic acid and Cl_2 gas is passed into the solution.

33. What is *dry ice* and how is it manufactured. Mention its uses.

34. How would you effect the following inter-conversions :

(a) $CO \rightleftarrows CO_2$

(b) $PbO \rightleftarrows Pb_3O_4$

(c) $SnCl_2 \rightleftarrows SnCl_4$

(d) $SnS \rightleftarrows SnS_2$

(e) $KCN \rightleftarrows KCNO$

Objective-type questions :

35. Pick up the correct answer :

(a) Water gas in mainly a mixture of

(i) CO and N_2 ; (ii) CO and H_2 ; (iii) CO and O_2 ; (iv) CO and H_2O ; (v) N_2 and H_2O.

(b) Lead monoxide is

(i) a basic oxide, (ii) a neutral oxide, (iii) an amphoteric oxide.

(c) When HF reacts with glass, the main product formed is

(i) NaF, (ii) CaF_2, (iii) H_2SiF_6, (iv) $NaF+SiF_4$, (v) SiH_4

(d) Glass is best described as

(i) A solid, (ii) A supercooled liquid, (iii) A solid solution, (iv) An occluded compound, (v) A colloid, (vi) Polymerised silica.

(e) Carbon disulphide burns with a blue flame on heating in air, producing

(i) Carbon disulphide vapour
(ii) CO_2 + sulphur vapour
(iii) $CO + SO_2$
(iv) $CO_2 + SO_3$
(v) $CO_2 + SO_2$.

36. Complete the following :

(a) The carbide ion in calcium carbide is ——.
(b) The important ore of tin is ——
(c) Mosaic gold is ——.
(d) —— is commercially known as *water glass*.
(e) White lead and red lead are...........respectively.
(f) The formula of potassium thiocarbonate is ——.
(g) Ammonium thiocyanate is also called ammonium ——.

CHAPTER XVI : GROUP VB ELEMENTS : THE NITROGEN FAMILY.

Essay-type :

16·1. Write a comparative account of the Gr. VB elements based on the following : (i) Electronic configurations, (ii) atomic volume, (iii) ionization potential, (iv) electronegativity, (v) acid-base character and (vi) nature of bonding.

16·2. Clearly describe the various points by which nitrogen differs from the rest of the Gr. VB elements. Discuss the reasons underlying such differences.

16·3. Describe the Haber process for the manufacture of ammonia, stressing on the physico-chemical principle involved. Describe its physical and chemical properties and account for its basicity and structure.

16·4 How are hydrazine, hydroxylamine and hydrazoic acid prepared ? Describe their more important properties and molecular structures. State their important uses.

16·5. Present a brief account of the oxides and oxyacids of nitrogen.

16·6. Discuss the physico-chemical principle underlying the Ostwald's process of nitric acid manufacture from ammonia. Describe the reaction of nitric acid with some metals and non-metals. How is ammonium sulphate manufactured in our country ?

16·7. How does phosphorus occur in nature ? How it is obtained from the natural sources ? Describe the different allotropic modifications of phosphorus and account for the difference in reactivity of the different allotropes on the basis of their structure.

16·8. Describe the preparation and properties of the oxides and oxyacids of phosphorus and give their structures.

16·9. Compare and contrast the hydrides of the Gr. VB elements. How is white phosphorus converted into red phosphorus and *vice versa* ? How would you distinguish between NH_3, PH_3, AsH_3, SbH_3 and BiH_3 ?

16·10. Briefiy describe the preparation, properties and structure of the halides and oxyhalides of phosphorus.

16·11. Starting from bismuth sulphide, Bi_2S_3, describe the preparation of the following : (i) Bi_2O_3, (ii) $BiCl_3$ (iii) $BiO(NO_3)$, (iv) sodium bismuthate ($NaBiO_3$) and (v) Bi_2O_5. Give the more important uses of bismuth compounds.

16·12. Describe the conditions under which the following substances react and write the balanced reactions, mentioning the products obtained : (a) calcium carbide and nitrogen (b) sodamide and N_2O ; (c) ammonia and NaOCl ; (d) nitrogen and oxygen ; (e) nitrite ion and iodide ; (f) $BiCl_3$ and $SnCl_2$ solutions.

16·13. Briefiy discuss the chemistry involved in the detection and estimation of P, As, Sb and Bi.

Short answer type :

16·14. (a) Account for the relative inertness of the nitrogen molecule.

(b) 'NH_3 is fairly basic but NF_3 is not'. — Explain.

(c) Hydrolysis of NCl_3 yields NH_3 and HOCl, but PCl_3 gives H_3PO_3 and HCl. — Why ?

(d) NCl_3 is rapidly hydrolysed in water but NF_3 is not. — Explain.

(e) The dipole moment of NCl_3 is much larger than that of NF_3. — Why ?

(f) "The NO-molecule can take part in coordination to a metal ion in three different forms."—Discuss.

(g) "The difference in the chemistries of nitrogen and phosphorus is mostly due to phosphorus possessing d-orbitals."—Discuss.

(h) Make a comparative study of HNO_2 and HNO_3 on the basis of the following : (i) acid strength, (ii) oxidation state of nitrogen, (iii) oxidising and reducing ability, (iv) structure of their ions.

(i) NH_3 is a good donor and forms many coordination complexes, but NF_3 or NCl_3 cannot act as donors, though all of them contain one lone-pair of electrons.

(j) Write chemical equations (properly balanced) to show the effect of heat on the following :

(i) a mixture of NH_4Cl and $NaNO_2$, (ii) NaN_3, (iii) $Cu(NO_3)_2$, (iv) NH_4NO_3, (v) $NaNO_3$.

(k) $AsCl_3$ (or any salt of arsenic), on treatment with HCl and metallic zinc, produces a gaseous substance which blackens a paper moistened with $AgNO_3$ soln. What is the gaseous compound ? Is it an oxidising agent ?

(l) Write balanced chemical equation of the reaction occuring when calcium phosphate is heated with nitric acid and ammonium molybdate.

(m) How can you obtain nitrogen from HNO_3 ? Or, prove that nitric acid contains nitrogen.

(n) Metallic copper does not dissolve in HCl but does so in HNO_3.—Why ?

(o) All ammonium salts behave as acids in liquid ammonia solution. —Explain.

(p) All amides behave as bases in liquid ammonia solution.—Justity or refute.

(q) Of the Gr. VB elements, only nitrogen can complete its 'octet' by gaining three electrons, but the others cannot do so.

—Explain why.

(r) Nitrogen forms only tricovalent species, while the other members can form both tricovalent and hexa-covalent species.

—Explain.

(s) In CH_4 and NH_3, the central elements, C and N are in the

sp^3-hybridised state ; yet the CH_4 molecule is tetrahedral, while NH_3 is somewhat pyramidal. Why ?

(t) Discuss the action of heat on NaH_2PO_4 under different conditions.

(u) An aqueous solution of ammonia reacts basic not because of the presence of ammonia itself with its own lone-pair of electrons, but because of OH^- ions generated in water. —Explain.

(v) The boiling point, surface tension and viocosity of liquid ammonia are much higher than the expected values. Why ?

(w) Liquid ammonia is a good solvent for ionic solids. Why ?

(x) Solutions of alkali and alkaline earth metals in liquid ammonia are strongly reducing in character. Explain.

(y) NCl_3 and PCl_3 are irreversibly hydrolysed in aqueous solutions, but $SbCl_3$ and $BiCl_3$ are reversibly hydrolysed. Explain why it so happens ?

(z) How can you distinguish between a nitrite and a nitrate, when present together ? State how you would determine nitrite in presence of a nitrate.

Objective type :

16·15. Answer by **yes** or **no.**

(a) HNO_2 is a stronger acid than HNO_3.

(b) HNO_2 is an oxidising agent under acidic conditions.

(c) H_3AsO_4 is weaker than H_3PO_4.

(d) NH_2OH is more basic than NH_3.

(e) BiH_3 is most stable and most basic among the hydrides of the Gr. VB elements.

(f) NH_4NO_3 behaves as an acid in liquid NH_3.

(h) Phosphorus occurs free in nature.

(i) H_2S is prepared by the action of HNO_3 on ferrous sulphide.

(j) Ammonia can be dried over P_2O_5 and conc H_2SO_4.

(k) White phosphorus is used in safety matches.

(l) For all the Gr. VB elements, the best way to attain the 'octet' in their valence-shell is by gaining three electrons.

(m) Among the members of the Gr. VB elements, the stability of the +5 oxidation state decreases with the increase in atomic number.

16.16. Fill up the blanks with appropriate words :

(a) — is formed when N_2O is passed over heated sodamide.

(b) Phosphorus never occurs in nature in the free state because it is —.

(c) Among the elements of Gr VB, the best way to attain the 'octet' in the valence-shell is to — — electrons.

(d) Among the heavier members of the Gr. VB, the pentavalent state becomes progressively unstable due to the operation of the —.

(e) Donor characteristic of the NH_3 molecule is due to the presence of a — of electrons in one of the — hybrid orbitals of nitrogen.

(f) The shape of the NH_3 molecule is —.

(g) The shape of the PX_5-molecules (X=Pl, Br) is —.

(h) The electrolysis of a cold concenterated solution of NaH_2PO_4 with platinum electrodes and high current density yields—.

(i) Boron nitride exists in two structural forms similar to — and —.

CHAPTER XVII : GROUP VIB ELEMENTS : THE OXYGEN FAMILY.

17·1. Why are the Gr. VIB elements called *the chalcogens* ? Write a comparative account of these elements based on the following : (i) Electronic configuration, (ii) atomic volume, (iii) ionization potential, (iv) electron affinity and electronegativity, (v) acid-base character and (vi) nature of bonding.

17·2. Describe clearly the various points of difference between oxygen and the rest of the members of the Gr. VIB elements. Explain the reasons underlying such differences,

17·3. Write a comparative account of the hydrides and halides of the Gr. VIB elements.

17·4. What are oxides and how are they classified ? Give a brief account of each class of oxide, pointing out their distinctive features.

17·5. How is ozone prepared in the laboratory ? Discuss the chemistry of ozone with special reference to its oxidising character, ozonide formation and molecular structure. Prove that ozone is an allotropic modification of oxygen.

17·6. How is sulphur isolated in the pure state ? Discuss the allotropy of elemental sulphur and state what happens when sulphur is gradually heated from room temperature up to its boiling point. Mention a few important uses of sulphur.

17·7. Briefly outline the principles of *two* methods of generating H_2S in the laboratory. Cite several cheimcal reactions to prove the reducing character of H_2S. Discuss the role of of H_2S in qualitative inorganic analysis.

17·8. Give a brief account of the oxides of sulphur and write down their structures.

17·9. Give an account of the oxyacids of sulphur. Write down their bond-structures.

17·10. Discuss the hybridisation scheme for the structure of the SO_2 and the SO_3 molecules.

17·11. Describe the contact process for the manufacture of sulphuric acid, laying stress on the physico-chemical principles involved. What is *oleum* ? State some major uses of H_2SO_4. Is there any other process for manufacturing H_2SO_4 ? Discuss the chemical reactions involved in that process.

17·12. (a) Give a brief account of the thionic acids and write down their structures. (b) Discuss the structure of the thiosulphate ion.

17·13. How are the peroxysulphuric acids obtained ? Discuss their role as powerful oxidants with some specific examples. Write down their structures and show that they are true derivatives of hydrogen peroxide.

17·14. Explain the following on the basis of oxidation-state and relative electronegativity of the different oxidation states involved : (a) H_2S can act as reducing agent only under normal conditions ; (b) SO_2 can act both as oxidising and reducing agents ; (c) SO_3 and H_2SO_4 can act only as an oxidising agent.

Short answer type :

17·15. Oxygen is a gas but sulphur is a solid. Why ?

17·16. The difference in atomic volume, electronegativity and the availability of the *d* orbitals in the valence-shell is responsible for most of the difference between oxygen and sulphur. Explain.

17·17. SF_6 is a very stable compound but SCl_6 or SBr_6 does not exist. Why ?

17·18. What is the reason of exceptional stability of the SF_6 molecule ? In what state of hybridisation is the sulphur atom present in it ?

17·19. Write down the structures of the tetrahalides of S, Se and Te, pointing out the state of hybridisation of the central element in each case.

17·20. Explain how the tetrahalides of S, Se and Te can act as monodentate donors.

17·21. SF_6 is not hydrolysed by water. SeF_6 is slowly hydrolysed and TeF_6 is completely hydrolysed in one day. Explain the reason underlying these differences in the behaviour of the three hexa fluorides.

17·22. The acidic character of the 'ous' acids of S, Se and Te, falls in the order $H_2SO_3 > H_2SeO_3 > H_2TeO_3$. Explain why it so happens.

17·23. H_2SO_4 is a stronger acid than H_2SO_3. Explain.

17·24. All the diatomic gases like H_2, N_2, F_2, Cl_2 etc. are diamagnetic, but oxygen gas is paramagnetic. Why ?

17·25. $\frac{1}{2}O_2(g)+2e \rightarrow O^{2-}(g)$; $\triangle H=236$ Kcals/mole. This shows that the formation of the oxide ion from molecular oxygen requires a large amount of energy and hence is an energetically unfavourable process ; yet many ionic oxides exist in stable form. Why ?

17·26. "The oxidising power of ozone is much greater in acid solutions than in alkaline solutions. Justify.

17·27. Sulphides of metals are more covalent than the corresponding oxides. Explain.

17·28. The formation of polysulphide ions is the manifestation of the strong Lewis base character of the S^{2-} ion. Discuss.

17·29. SO_2 can act both as an oxidising agent and a reducing agent. Explain, how it so happens ?

17·30. The structure of the $S_2O_3^{2-}$ ion can be derived from that of the SO_4^{2-} ion. Discuss with illustrations.

17·31. The structure of the SO_3^{2-} ion is pyramidal, but the S—O bonds have considerable double bond character. Explain how it can be so.

17·32. The acidity of the hydrides H_2S, H_2Se, H_2Te increases from H_2S to H_2Te, though electronegativity decreases in that direction. Explain.

17·33. The structure of the SO_4^{2-} ion is tetrahedral with considerable double bond characters induced in S—O bonds. Comment.

17·34. Though of higher molecular weight, H_2S is a gas while H_2O is a liquid at ordinary temperature. Why ?

17·35. F_2O and F_2O_2 are better represented as fluorides of oxygen than as oxides of fluorine. Comment.

Objective type :

17·36. Answer by 'yes' or 'no' :

(a) H_2S is a stronger acid than either H_2Se or H_2Te.

(b) H_2SO_3 is a weaker acid than H_2SO_4.

(c) SF_4 is more covalent than SCl_4.

(d) SF_6 is stabler than SF_4.

(e) The AX_4-type tetrahalides of S, Se and Te have one lone-pair in the sp^3d-hybrid orbital of S, Se or Te.

(f) Hydrolytically, TeF_6 is more stable than either SeF_6 or SF_6.

(g) Except with fluorine, oxygen does not exhibit positive oxidation state.

(h) Oxides of metals are more ionic than the corresponding sulphides.

(i) Ozone is a more powerful oxidant in alkaline medium than it is in an acid medium.

(j) In an aqueous solution of hydrogen sulphide, H^+, HS^- and S^{2-} ions are in equilibrium with undissociated H_2S.

(k) SO_2 can act as a reducing agent only and not as an oxidant.

(l) Peroxydisulphate can oxidise manganous salts to the permanganate stage only in the presence of Ag^+ ions.

17·37. Fill up the gaps with appropriate words :

(a) —— is the most abundant element in the earth's crust.

(b) All the Gr. VIB elements are —— elements, with an outermost electronic configuration of —— .

(c) In the solid state, sulphur exists in —— allotropic modifications known as —, — and —— modifications.

(d) In the Gr. VIB elements, the atomic volume —— with the increase in atomic number.

(e) The ionization potential of the Gr. VIB elements decreases with the increase in atomic number because of the increase in —— and the ——— of the inner layer of electrons.

(f) The acidity of the hydrides —— with the increase in atomic number.

(g) The acidic character of the RO_2-type of oxides —— with the increase in atomic number.

(h) The best way for the atoms of Gr. VIB elements to attain octet in the valence-shell is to —— two electrons.

(i) The shape of the H_2O molecule is —— with two lone-pairs remaining in two of the —— hybridised orbitals.

(j) Thermal stability and covalent character of the hydrides of Gr. VIB elements —— from S to Ts.

(k) The S_2Cl_2 is a —— molecule with the sulphur in the —— state of hybridisation.

(l) The SO_3 molecule has a —— shape.

CHAPTER XVIII : ELEMENTS OF GROUP VII B : THE HALOGENS.

Essay-type questions :

1. Name the members of the halogen family and give their general electronic configuration. Why are the elements so called ? Discuss the properties of the halogens which are consistent with their electronic configurations. How far it is justified to include manganese in the same group as the halogens ?

2. Give a comparative account of the properties of the halogens as well as their principal compounds. How does fluorine differ from the other halogens ?

3. Name two minerals containing fluorine and state their compositions. Describe the preparation and properties of fluorine,

pointing out the difficulties which confronted the earlier chemists in the isolation of the element. Compare and contrast the properties of fluorine with those of other halogens.

4. Describe the preparation of anhydrous hydrogen fluoride and mention its important properties and uses.

5. Compare the properties of the four halogen hydracids and mention their important uses.

6. Describe briefly a method used for the large scale preparation of chlorine. Discuss the important properties and uses of chlorine. How is chlorine used in the preparation of (i) bleaching powder and (ii) potassium chlorate ?

7. How is hydrochloric acid manufactured by the synthetic method ? How can you prepare very pure hydrogen chloride in the laboratory ? Discuss the mechanism of combination of H_2 and Cl_2 in the presence of light.

8. Describe how you would establish the volumetric composition of hydrochloric acid, both by analytical and synthetic methods.

9. Give a short account of the preparation and properties of the oxides and oxyacids of chlorine and discuss their structures.

10. Describe the methods of manufacturing bromine from *bittern* and from sea-water. Starting from bromine, how you would prepare (a) potassium bromate and (b) gaseous hydrogen bromide ?

11. How is hydrobromic acid manufactured ? Mention the uses of hydrobromic acid and one of its important salts.

12. How the oxides and oxyacids of bromine are prepared ? Mention their properties and discuss their structures.

13. How is iodine obtanined on a large scale ? Mention the important properties and uses of iodine.

14. Give a short account of the preparation, properties and structures of the oxyacids of iodine.

15. Write down what you know about electropositive iodine and its compounds. What evidences can you put forward to prove the existence of the halogen as the positive ion in these compounds ?

16. Explain and illustrate what are inter-halogen compounds and the polyhalides. How are they formed ? Write down the structures of different types of inter-halogen compounds. How would you account for the nature of binding force in these compounds ?

Short questions :

17. Write short notes on :

(a) Fremy's salt, (b) Solvent action of liquid HF, (c) Oxides of fluorine, (d) Photochemical combination of H_2 with Cl_2, (e) Chlorates and perchlorates, (f) Periodic acids and periodates, (g) Elecropositive iodine, (h) Interhalogen compounds, (i) Polyhalides, (j) Pseudo-halogens or halogenoids.

18. How are the following substances best prepared ? Mention their important uses :

(a) Potassium chlorate, (b) Potassium perchlorate, (c) Potassium bromide, (d) Iodic acid, (e) Iodine monochloride.

19. What happens when : (Give the conditions and equations of the reactions).

(a) Chlorine reacts with caustic soda solution.

(b) Fluorine reacts with caustic soda solution.

(c) Hydrofluoric acid is kept in a glass bottle.

(d) Chlorine is passed over precipitated HgO, which was previously heated to 300°C.

(e) Precipitated HgO is treated with chlorine water.

(f) Chlorine dioxide reacts with caustic soda solution.

(g) Sodium chlorate is added to a solution of potassium iodide.

(h) Potassium chlorate is separately warmed with conc. HCl and conc. H_2SO_4.

(i) Iodine reacts separately with stannous chloride and sodium thiosulphate.

(j) Iodic acid is gradually heated upto 200°C.

(k) Iodic acid reacts with an acidified solution of potassium iodide.

(l) Potassium iodide solution is treated with HgO.

(m) Bromine reacts with sodium carbonate and sodium thiosulphate separately.

(n) Iodine reacts with conc. HNO_3.

(o) Iodine reacts with potassium chlorate.

20. Explain why

(a) Fluorine differs widely from the other halogens in its properties.

(b) There is a gradual change from non-metallic to metallic character as we move down from fluorine to iodine.

(c) Fluorine always acts as a uninegative ion, whereas the other halogens exhibit negative as well as positive oxidation states.

(d) Halogens act as oxidising agents and their oxidising power decreases as we move from fluorine to iodine.

(e) At 15°C, HF is a liquid, while HCl is a gas.

(f) Although fluorine is the most electronegative halogen, it forms the weakest of all the halogen hydracids.

(g) Compound of the composition KHF_2 (bifluoride) is known, but $KHCl_2$ or $KHBr_2$ are not known.

(h) Polyhalide ions like I_3^-, Cl_3^- exist, but F_3^- does not exist.

(i) Fluorine exhibits a covalency of one unit only, whereas the other halogens show covalency ranging from 1 to 7.

Objective-type questions :

21. State which one of the following is correct :

(a) The high oxidising power of fluorine is due to its

(i) high electron affinity

(ii) high heat of dissociation and low heat of hydration

(iii) high heat of hydration and low heat of dissociation

(iv) high heat of hydration and high heat of dissociation.

(b) Fluorine is not prepared by the general method of preparing other halogens because

(i) HF can be easily oxidised

(ii) HF is not easily oxidised

(iii) HF is highly poisonous

(iv) HF is a bad conductor of electricity.

(c) Hydrogen fluoride should not be stored in glass bottles, because it

(i) etches glass, (ii) paints glass, (iii) is exposed to light.

(d) If iodine solution stains the clothes, the solution that can be used to remove the stains is

(i) Sodium chloride, (ii) Sodium bromide, (iii) Sodium thiosulphate, (iv) Sodium tetrathionate.

(e) The halogens are chemically similar because

(i) the atomicity of each element is 2

(ii) their outermost electrons have the same quantum number

19·4. Briefly discuss the nature of variation of the following properties among the first transition series of elements : (a) electronic configuration, (b) Atomic volume and density, (c) atomic and ionic radii, (d) ionization potential and electronegativity.

19·5. "The alkali and the alkaline earth metals have the same outermost electronic configuration (ns^1, ns^2) as that of the transition elements. But the transition elements are far less reactive than the alkali or alkaline earth metals". Comment.

19·6. Define ionization energy and ionization potential. Discuss the variation of ionization energy along the first transition series with the increase in atomic number.

19·7. "The fairly high values of the electrode potentials of the transition elements suggest that they should be good reducing agents ; but they are actually not good reducing agents." Comment.

19·8. Discuss the reasons underlying the existence of more than one valency-states in the cases of the transition elements. Illustrate your answer with specific examples.

Short answer type :

19·9. (a) Compounds of s- and p-block elements are generally colourless, but most compounds of the transition metals are coloured. Why ?

(b) Coming after vanadium ($3d^3 4s^2$), chromium should have the electronic configuration $3d^4 4s^2$; instead, it possesses the electronic configuration $3d^5 4s^1$. Explain why it so happens.

(c) Why does copper (At. no.=29) has the valence-shell configuration of $3d^{10} 4s^1$ and not $3d^9 4s^2$?

(d) According to the definition, Cu and Zn are not *true transition elements* ; but many authors prefer to include them among the transition elements. Explain the underlying reasons for doing so.

(e) Most of the transition metals and many of their compounds are paramagnetic. Why ?

(f) All transition metals exhibit variable valency. Why ?

(g) Transition metals have strong complex-forming tendency. Why ?

(h) The values of the ionization potential of the elements of the first transition series are reasonably constant. Comment.

(i) Ti^{+3}, V^{+4}, Mn^{+2} and Cu^{+2} are paramagnetic, but Ti^{+4}, V^{+5}, Mn^{+7} and Cu^{+1} are diamagnetic. Explain.

(j) Cu^{+2} compounds are coloured, but Cu^{+1} compounds are colourless. Why ?

(k) Manganese is the most versatile element among the members of the first transition series. Comment.

Objective type :

19·10. Answer by **yes** or **no** :

(a) In the case of transition elements, the general electronic configuration is $ns^2\ (n-1)\ d^{1-9}$.

(b) Copper has the valence-shell electronic configuration of $3d^9 4s^2$.

(c) The different oxidation states of titanium (Z=22) are +2 and +4 only.

(d) All Cu^{+1} compounds are coloured.

(e) Cu^{+2} compounds are paramagnetic.

(f) Coordination complexes of Ni (II) can be diamagnetic or paramagnetic.

(g) All transition metals are highly reactive.

(h) Most transition elements exhibit good catalytic properties.

(i) Copper can liberate hydrogen from non-oxidising acids, but zinc can not do so.

19·11. Fill up the gaps with appropriate words :

(a) In transition elements, the *differentiating electrons* lie in the —— level.

(b) The transition metal ions can act as good —— centres because of their comparatively —— charge and —— ionic radii.

(c) Most of the transition metal compounds are coloured because of the presence of — — electrons in them.

(d) Co^{+3} complexes are diamagnetic, as the Co^{+3} ion has no — electrons.

(e) The structure of $[Ni(CN)_4]^{2-}$ is —, but that of $[Ni(NH_3)_4]^{+2}$ is — .

(f) The compound $CoCl_3.4NH_3$ can exist as — isomers. They are known as the — and the — isomers.

(g) When excess ammonium hydroxide is added to a solution of a Cu(II) compound, a deep — colour is formed due to the formation of the coordination complex — .

(h) The atomic volume of the transition metal atoms does not increase much with the increase in atomic numbers, because the incoming electrons are added to the — level.

TITANIUM

Essay-type :

1. How does titanium occur in nature ? Describe one process of extraction of titanium from one of its ores. How is titanium purified ? Discuss the uses of the metal and its compounds.

2. Starting from a titanium ore, how will you prepare the following compounds : (i) TiO_2, (ii) $TiCl_4$, (iii) $TiBr_4$, (iv) $TiCl_3$ and $Ti_2(SO_4)_3$, (v) TiO, and $TiCl_2$.

Short answer type :

3. (a) Write down the electronic configuration of the titanium atom. (b) Account for the occurrence of the +2, +3 and +4 oxidation states of this metal. (c) Which oxidation state is most stable and why ?

Objective-type :

4. **Answer by yes or no :**

(a) TiO is more basic than TiO_2.

(b) $TiCl_3$ is a stronger reducing agent than $TiCl_4$.

(c) $TiCl_3$ is more readily hydrolysed than $TiCl_4$.

(d) Ti^{+3} is a d^1-system and Ti^{+4} is a d°-system.

5. **Fill up the gaps with appropriate words :**

(a) $TiCl_2$ is more — than $TiCl_3$.

(b) Ti (III) compounds are paramagnetic, while the Ti (IV) compounds are — .

(c) When dissolved in conc. HCl, $TiCl_4$ yields anionic complexes of the formula — and — .

(d) All Ti (III) compounds have a strong — property, as they have a strong tendency to change to Ti (IV) compounds.

6. **Put tick mark on the correct answer :**

(a) In the Kroll process, $TiCl_4$ vapour is reduced by : (i) Zn-metal ; (ii) Fe-metal ; (iii) Mg-metal.

(b) In the Van Arkel method of purifying titanium, the compond used is : (i) TiO_2 ; (ii) $TiCl_4$; (iii) TiI_4 ; (iii) TiI_3.

(c) The most stable oxidation state of titanium is the : (i) +3 state ; (ii) +2 state ; (iii) +4 state.

VANADIUM

Essay-type :

1. Name the important ores of vanadium. How is vanadium obtained from its ores as : (i) Ferrovanadium and (ii) the pure metal ? State the uses of vanadium metal and its alloys.

2. Starting from an ore of vanadium, how will you obtain the following : (i) V_2O_5, (ii) NH_4VO_3, (iii) $VOSO_4$, (iv) VCl_4, (iv) VCl_3 and (v) VCl_2 ? State the uses of vanadium compounds.

Short answer type :

3. (a) Write the electronic configuration of the vanadium atom. (b) What are the possible oxidation states of vanadium ? Give the electronic configurations of all of them.

4. (a). Which one is the most stable oxidation state of vanadium and why ?

(b) Pentavalent vanadium compounds are strong oxidising agents. Why ?

(c) V(III) and V(II) compounds are strong reducing agents. Why ?

Objective type :

5. **Fill up the gaps with appropriate words :**

(a) The alloy of vanadium with iron, containing 30 – 45% of vanadium, is known as — .

(b) When a colourless V^{+5} compound is reduced with zinc, it first turns blue, then — and finally — .

(c) Violet coloured aqueous solutions of V^{+2} salts change to green due to oxidation of V^{+2} to V^{+3} ion with the liberation of hydrogen. Hence, V^{+2} compounds are strong — agents.

CHROMIUM

Essay-type :

1. How does chromium occur in nature ? Describe the process of extraction of chromium from chromite. State its properties and describe the chief uses of the metal and its alloys.

2. Starting from chromite, how would you obtain the following compounds : (i) K_2CrO_7, (ii) K_2CrO_4, (iii) CrO_2Cl_2, (iv) CrO_3, (v) Chrome alum, (vi) $Cr_2(SO_4)_3$, (vii) $CrCl_2$? State some of the uses of these compounds.

Short answer type :

3. Write notes on the preparation and uses of (i) chrome yellow, (ii) chrome green, (iii) chrome red, (iv) zinc yellow and (v) Guigrét's green.

4. Write the electronic configuration of the chromium atom and explain why it is so.

5. What are the possible oxidation states of chromium ? Give the electronic configurations of each of them.

6. Which oxidation state of chromium is most stable ?

7. The equivalent weight of $K_2Cr_2O_7$, as an oxidising agent in acid solution, is $\frac{1}{6}$th its molecular weight. Comment.

8. The blue compound generated by the action of H_2O_2 on an acidified solution of a dichromate is not a peroxychromic acid, but a peroxide of chromium. Comment.

9. $K_2Cr_2O_7$ is a powerful oxidising agent in acid solution. Comment.

Objective type :

10. *Fill up the gaps with appropriate words :*

(a) The ground state electronic configuration of the chromium atom is $3d^54s^1$ and not $3d^44s^2$, because of the special stability of the —— orbitals.

(b) $CrCl_3$ forms three aqueous complexes of the formulae —, — and $[Cr(H_2O)_3Cl_3]^\circ$.

(c) All chromous salts are strong — agents.

(d) A chromium-iron alloy, containing about 60-70% of chromium, is known as — .

(e) $CrCl_2$ is more — than $CrCl_3$.

11. *Put tick marks over the correct answers :*

(a) Potassium dichromate is widely used in chemical analysis as (i) a reducing agent, (ii) a complexing agent, (iii) an oxidising agent.

(b) The nature of CrO_3 is (i) acidic, (ii) basic, (iii) neutral.

(c) K_2CrO_4 can be converted to $K_2Cr_2O_7$ by the action of (i) a base, (ii) an acid, (iii) by heating.

(d) The compound CrO_2Cl_2 is (i) ionic, (ii) covalent.

MANGANESE

Essay-type :

1. How does manganese occur in nature ? Describe the process of extraction of manganese from its chief ore. Describe the important properties and uses of manganese metal and name some of its useful alloys.

2. Starting from pyrolusite, how can you prepare the following : (i) Pure MnO_2, (ii) $KMnO_4$; (iii) manganic alum, (iv) $MnSO_4$, (v) $MnCl_2$. State some of the uses of these compounds. What is meant by the term 'available oxygen' of pyrolusite ? How can you determine it ?

3. Describe the process of manufacturing $KMnO_4$ from pyrolusite. Discuss its various uses, stressing on its use as an oxidising agent in chemical analysis.

4. $KMnO_4$ can not be used as a primary standard substance. Why ? "The equivalent weight of $KMnO_4$ is dependent on the nature of the reaction medium." Discuss the statement with relevant examples.

Short answer type :

5. Answer the following :

(a) Write down the electronic configuration of the manganese atom in the ground state.

(b) Indicate the possible oxidation states that manganese can attain, and give the valence-shell electronic configurations of all such states.

(c) Which oxidation state of manganese is most stable and which one is most unstable ?

(d) The conversion of MnO_4^{2-} (manganate) into MnO_4^- (permanganate) is not an oxidation – reduction reaction, but is a disproportionation process. Comment.

(e) $KMnO_4$ is not a primary standard substance. Why ?

Objective-type :

6. *Fill up the gaps with appropriate word* :

(a) Coming after chromium ($3d^5 4s^1$), the valence-shell electronic configuration of manganese is —, and not $3d^6 4s^1$.

(b) When any manganese compound is fused with an alkaline flux and an oxidising agent (say, Na_2O_2 or KOH/KNO_3 mixture), — is produced.

(c) The valency of manganese in manganates is — .

(d) On treatment with an acid, manganates are converted to — by a — reaction.

(e) Manganese resembles chlorine only in the — oxidation state.

(f) Permanganates and perchlorates are — with each other.

7. Put tick marks on the correct answer :

(a) In oxidimetric methods, $KMnO_4$ is used as a (i) primary standard, (ii) secondary standard reagent.

(b) Compared as an oxidising agent, $KMnO_4$ is (i) less powerful than, (ii) more powerful than, (iii) equally powerful as $K_2Cr_2O_7$.

(c) Mn^{+4} ions are (i) stable, (ii) unstable in aqueous solution.

(d) MnO is (i) more basic, (ii) less basic than MnO_2.

(e) Mn_2O_7 is (i) most acidic, (ii) least acidic of all oxides of manganese.

CHAPTER XX : IRON, COBALT AND NICKEL ; THE METALS OF THE EIGHTH GROUP.

Essay-type questions :

1. Compare the physical and chemical properties of the metals of the iron group, as well as of their principal compounds.

2. Compare and contrast the physical and chemical properties of chromium, manganese and iron, as well as of their important compounds.

3. Name the important ores of iron and mention their chemical formulae. How is cast iron manufactured ? Discuss, with the help of a rough sketch, the reactions which take place at the various parts of the blast furnace. How the by-products, available in the process, are utilised ?

4. Describe the manufacture of cast iron, mentioning the raw materials required and the purpose of each ingredient of the charge.

5. Discuss the difference in composition and properties of the varieties of cast iron. How is cast iron converted into wrought iron? Mention the uses of cast iron and wrought iron.

6. What is the difference in composition between cast iron, wrought iron and steel? Describe briefly the Bessemer process of manufacturing steel. What is the importance of basic Bessemer process?

7. Give a short account of the different processes of preparing steel from cast iron, indicating briefly the chemical reactions involved in each.

8. Describe the open-hearth process of manufacturing steel from cast iron. Compare and contrast this process with the Bessemer process, mentioning the advantages of one over the other.

How is very high quality steel prepared by the electric furnace process?

9. What are special steels and how are they prepared? Name some important special steels and mention their uses.

10. How is chemically pure iron prepared? Give an account of its allotropic modifications and of its general physical and chemical properties.

11. What is meant by *passivity* and *rusting* of iron? State briefly the views advanced to account for them. What means are usually adopted to prevent rusting of iron?

12. Give an account of the important compounds of nickel and cobalt, with special reference to the points of similarity and difference between the chemical properties of the two elements.

13. How does cobalt occur in nature? State the chemistry involved in the extraction and refining of the metal from its ores. State the uses of cobalt. How is cobalt salt, free from traces of nickel, are obtained?

14. What are the chief sources of nickel? How is pure nickel obtained from its ores? Write down the important uses of nickel. Discuss the methods available for the detection and estimation of the metal.

15. How is nickel carbonyl prepared? State its important properties and structure. What is the valency of the metal in this compound? How would you prepare a specimen of pure nickel salt from nickel containing cobalt as an impurity, and a pure cobalt salt from cobalt containing nickel as an impurity?

16. What are cobaltammines? Describe their general methods of preparation. Show how by gradual substitution of ammonia by negative atoms or groups in the cobaltammine molecule, a series of new complexes with progressive variation in the charge of the complex ion may arise.

Short questions :

17. Write short notes on :

(a) Cowper stove, (b) Blast furnace gases and slags, (c) Puddling process of preparing wrought iron, (d) Annealing or tempering of iron, (e) Case-hardening of wrought iron, (f) Spiegeleisen, (g) Bessemer converter, (h) Thomas-Gilchrist process, (i) Duplex process, (j) Lintz-Donawitz process, (k) Alloy steels, (l) Allotropy of iron, (m) Passivity of iron, (n) Rusting of iron, (o) Iron alums, (p) Ferrates and ferrites, (q) Prussian blue and Turnbull's blue, (r) Cobaltammines, (s) Cobaltinitrites, (t) Nickel carbonyl.

18. How are the following substances prepared and what are their uses :

(a) Anhydrous ferric chloride, (b) Ferric alum, (c) Mohr's salt, (d) Potassium cobaltinitrite, (e) Nickel carbonyl, (f) Iron penta-carbonyl, (g) Sodium ferrate, (h) Sodium nitroprusside, (i) Ferric sulphate, (j) Potassium ferrocyanide, (k) Smalt, (l) Nickelic oxide.

19. Starting from iron, how would you prepare :

(a) ferric oxide, (b) anhydrous ferrous chloride, (c) anhydrous ferric chloride, (d) ferrous sulphate, (e) Mohr's salt?

20. Mention the tests you would perform to distinguish between ferrous and ferric salts.

21. Discuss the methods used for the qualitative separation of nickel from cobalt.

22. Discuss the influence of addition of (a) carbon and (b) manganese on the quality of iron.

23. What happens when : (Give the conditions and equations of the reactions) :

(a) Moist iron pyrites is exposed to air.

(b) Ferrous sulphate is strongly heated.

(c) Ferric oxide is fused with sodium carbonate.

(d) Ferrous sulphate is boiled with conc. H_2SO_4.

(e) A solution of ammonium oxalate is gradually added to a solution of a ferric salt.

(f) Chlorine gas is passed through a suspension of ferric hydroxide in caustic soda solution.

(g) Potassium cyanide solution is gradually added to a solution of a ferrous salt.

(h) Potassium ferrocyanide is strongly heated.

(i) Potassium ferrocyanide is warmed with dilute and conc. H_2SO_4 separately.

(j) Potassium ferrocyanide is treated with HNO_3.

(k) Potassium ferricyanide is treated with a solution of hydrogen peroxide in alkaline medium.

(l) Potassium ferrocyanide solution is added to a solution of ferric chloride.

(m) A solution of cobaltous salt reacts with a solution of ammonium thiocyanate.

(n) Potassium cobalticyanide is heated with conc. H_2SO_4.

(o) A solution of cobaltous salt is treated with a solution of potassium nitrite in presence of acetic acid.

(p) A solution of potassium cyanide is added in excess to a solution of a nickel salt.

(q) Iron pentacarbonyl reacts with sulphuric acid.

(r) Iron enneacarbonyl is heated.

24. Explain why—

(a) Limestone is added to the charge in the blast furnace to prepare cast iron.

(b) Cowper stove is employed in conjunction with a blast furnace in the metallurgy of iron.

(c) The lining of Bessemer converter is often made of lime and magnesia.

(d) Fe(III) salts are more stable than Co(III) and Ni(III) salts.

(e) Spiegeleisen is used in making steel.

THE SOLID STATE : SOME IMPORTANT AND USEFUL ASPECTS

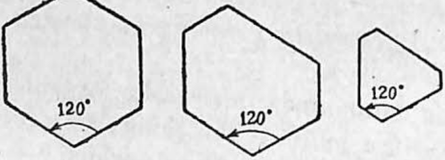
The gaseous state is characterised by the presence of isolated atoms or molecules moving at random and having very little attraction for each other. Hence, the gases are highly compressible and have no definite volume or shape of their own. In the liquid state, the constituent particles (molecules or atoms) possess random motion to a much lesser degree, lie much closer to each other and the force of attraction between the particles is of a considerably higher order of magnitude. Hence, the liquids are much less compressible than the gases and have their own volumes (for a given mass). But, the force of attraction among the constituents of a liquid is not strong enough to impart sufficient rigidity so as to maintain a definite shape. Hence, the liquids do not have a shape of their own but take the shape of the container in which they are kept. On the other hand, in the solid state, the constituent particles (atoms, ions, molecules) lie very close to each other, held together by strong attractive forces and occupy definite positions with respect to one other. The most important characteristic properties of the solids, arising out of the above structural factors are (i) *rigidity*, (ii) *very low compressibility* and (iii) *characteristic geometry* manifested in their tendency to form crystals.

Since, majority of the inorganic compounds (also many organic compounds) are solids, and also because most of the things we see around us in nature and many of the materials and devices which we use in our daily life are solids, the study of the solids, aimed at a possible correlation of their important properties with their characteristic structural features is of immense importance and utility. In fact, the recent advances made in the field of physics and chemistry of solids have been instrumental in bringing about several major break-through in contemporary science and technology. A single example in the form of discovery and uses of **transistors** (made from doped germanium or silicon) will be sufficient to illustrate this point.

Crystalline solids Vs Amorphous solids.

Solids can be broadly divided into (a) *crystalline* and (b) *amorphous* materials. Familiar examples of crystalline solids are sugar, common salt, alum and quartz, while those of amorphous materials are glass, rubber and various types of plastics. As solids, both the crystalline and the amorphous materials have many common properties. Both of them are *rigid*, have their *own characteristic volume* and are *very little compressible*. However, **the crystalline materials are distinguished by their existence in characteristic geometric forms which are the outward manifestations of the highly ordered and periodic arrangement of the atoms, ions or molecules constituting the crystal.** The amorphous solids do not possess similar *ordered* and *periodic* arrangement of the structural units. Another point of difference between the amorphous and crystalline solids lie in the fact that, the properties of the amorphous materials (such as, mechanical strength, electrical conductivity etc.) are same throughout the bulk of the material in all directions and hence, the amorphous solids are *isotropic*. But, in a crystalline solid, these properties usually depend on the direction along which they are measured. In other words, the crystalline solids are not isotropic like the amorphous materials ; they are *anisotropic* in nature. *Anisotropic nature of a crystalline solid definitely indicates the presence of highly ordered structural units in it.* The present discussion will include only the crystalline solids and the amorphous materials will not be dealt with.

Crystalline solids : A substance is classified as crystalline if its constituent structural units (atoms, ions or molecules) are arranged in a definite pattern and this pattern is repeated continuously. This gives rise to a definite geometrical configuration which is a specific characteristic of that particular crystalline substance. A crystal is thus, a symmetrical body generally bound by several plane surfaces which are called *faces*, and the line along which two such faces meet one another is known as an *edge*. An *interfacial angle* is the angle between two intersecting faces (Figure 1.). The domain of *crystallography* consists mainly of the study of the definite geometrical arrangements and patterns occuring in different types of crystals and of the properties of crystalline solids associated with a particular structural pattern. The basic concepts and laws, briefly outlined below, are essential for understanding the subject of crystallography.



(a) (b) (c)

Fig. 1

(i) **Steno's Law of the constancy of interfacial angles.**

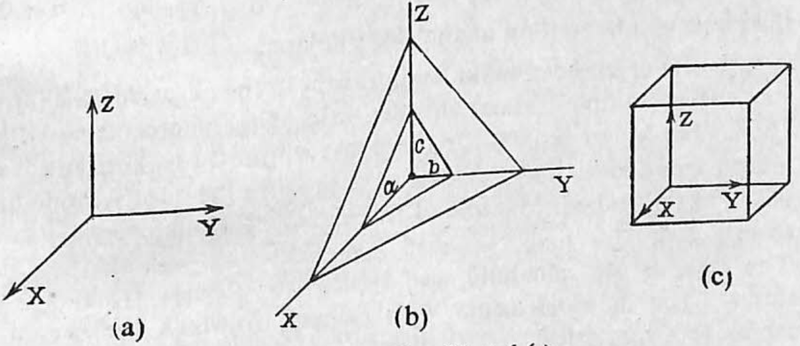
"The angles between the corresponding faces of various crystals of the same substance are constant." The overall shapes of the crystals of a particular substance may be differently developed depending on the conditions of crystal-growth, but the interfacial angles between two corresponding faces will always be constant. In

figure 1, though the crystals have different shapes, the angle between the same two faces is the same in all the three cases.

The foundation of crystallography was laid in 1784 by Haüy when he observed that the external geometrical form of any crystal is a reflection of the inner regular order of the arrangements of the structural units. According to this law, which is found to be almost universally true, a crystal is made up of a large number of smaller crystals, each of which is an exact replica of the original bigger crystal. Such smallest crystal, by the repetition of which the original crystal can be formed, is termed as the *unit cell.* It represents the ultimate structural unit of the crystal.

The concept of crystallographic axes : The geometry of a crystal is referred to a set of three arbitrarily chosen non-planar coordinate axes [Fig. 2(a)] known as the crystallographic axes. These may or may not coincide with the principal edges of the crystal. These three axes may be mutually perpendicular to each other, or may be at any other desired angle. In the case of a cubic crystal, the crystallographic axes coincide with the three mutually intersecting and perpendicular edges as shown in Fig. 2(c).

Let us now focus our attention on any one face of a cubic crystal which cuts the three crystallographic axes, this face being considered as the standard face [Fig. 2(b)]. The length of the intercepts made by the face on the X, Y and Z axes are a, b and c respectively, which are the standard intercepts. If any other face cuts intercepts of x, y and z on the three axes then, $x : y : z = ha : kb : lc$, where h, k and l are simple integers like 1, 2, 3 etc. Thus, *the intercepts cut on a given axis by all faces of a crystal bear a simple ratio to one another.* This is a simple statement of **Haüy's Law of rational intercepts** and it is an outcome of the ordered existance of the atoms or ions in a crystal.



(a) (b) (c)

Figs. 2(a), (b) and (c)

Miller indices : For each crystallographic axis, an unit of length can be so chosen that the intercepts of all other faces on that axis may be expressed as small whole numbers. This unit of length may or may not be the same for the three different axes, but the ratios of the units [($a: b: c$), Fig.2(b)] on the different axes will be the same for each and every crystal of any particular substance. If, now, a face makes intercepts of A, B and C on the X, Y and Z axes respectively (where the standard intercepts are a, b and c), so that $a : b : c = 2a : b : 2c$ then, in terms of the standard, the ratio of the two sets of intercepts is $2 : 1 : 2$. These ratios define a particular face or plane of the crystal. For the sake of convenience, the reciprocals of the coefficients of a, b and c are used to denote a particular plane and when necessary, the ratio is multiplied by the least common multiple to obtain integral values. Thus, the Miller indices of the plane denoted by the intecept ratio $2a : b : 2c$, i.e. $2 : 1 : 2$ will be $\frac{1}{2} : 1 : \frac{1}{2}$, i.e. $1 : 2 : 1$. This face of the crystal is denoted as the (1 2 1) plane. If we consider another such plane parallel to the X-axis, it will cut the X-axis at infinity and the ratio of the intercepts will be $\propto : b : 2c$ and the Miller indices will be $\frac{1}{\propto} : 1 : \frac{1}{2}$, i.e. $0 : 2 : 1$ and the plane will be designated as the (0 2 1) plane. A plane perpendicular to the X-axis and parallel to the Y and Z axes will have intercepts $a : \propto : \propto$ will have Miller indices $1 : \frac{1}{\propto} : \frac{1}{\propto}$, i.e. $1 : 0 : 0$ and the plane will be written as the (1 0 0) plane.

A face of a crystal can make an intercept in the negative direction of an axis (for example X-axis) and the ratio of the intercepts may be $-a : b : c$; the Miller indices for the plane will be 1 1 1, the bar above any integer will denote that the intercept is cut on the negative side of the axis. Miller indices of some of the planes of a cubic crystal are shown in Fig. 3.

The crystals we generally see appear to possess symmetrical structures. The main elements with respect to which the crystals appear to be symmetrical are (i) plane of symmetry (ii) axis of symmetry and (iii) centre of symmetry.

(i) **Plane of symmetry :** It is an imaginary plane which can divide the crystal into two halves such that one half is the mirror image of the other. A crystal may possess more than one plane of symmetry [Fig. 4 (a)].

(ii) **Axis of symmetry :** If rotation of a crystal about a line through the centre of the crystal by any angle results in an orientation of the crystal that is superimposable on the original, **the axis is called**

an axis of symmetry or, more precisely, **a rotational axis of symmetry.** If the angle through which the crystal must be rotated in order to secure the superimposable image be denoted by θ° then, the crystal is

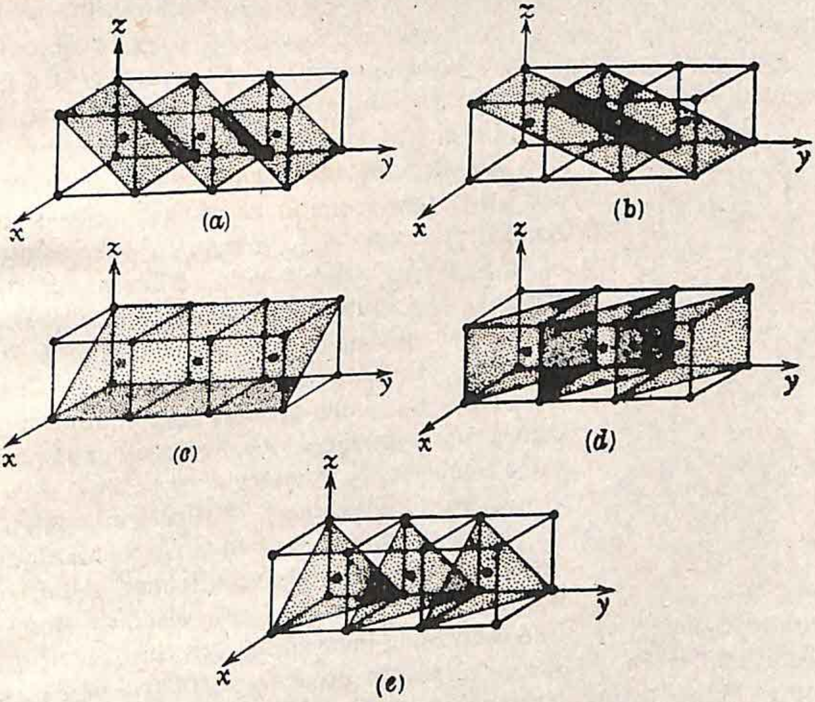


Fig. 3

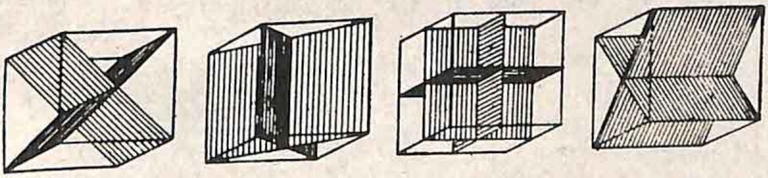


Fig. 4(a) Different planes of symmetry of a cubic crystal

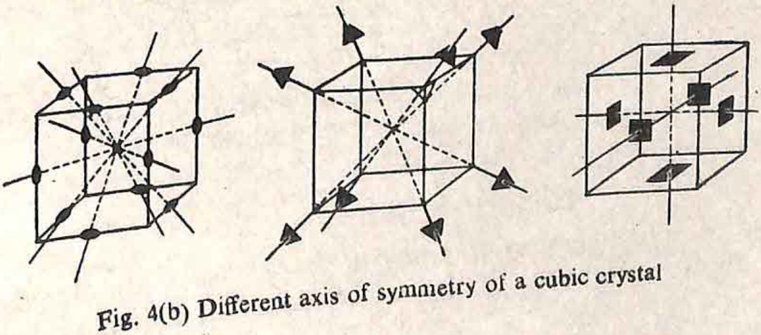
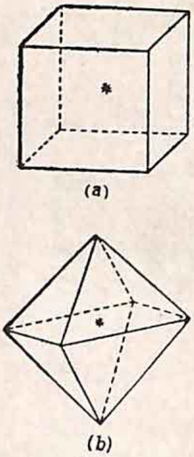


Fig. 4(b) Different axis of symmetry of a cubic crystal said to possess a 360°/θ-fold rotational axis. Depending on the number of times the crystal appears unchanged on a complete revolution through 360°, the crystal is said to possess two, three, four and six-fold axis of symmetry denoted by C_2, C_3, C_4 and C_6 respectively (Fig. 4b).

Centre of symmetry : A crystal is said to possess a centre of symmetry if every face has another identical face at an equal distance from the centre (Fig. 4c).



Fig, 4(c) centre of symmetry (a) of cube ; (b) of an octaledrox

The **elements of symmetry** of a crystal are the total number of its planes of symmetry, axes of symmetry and centre of symmetry. Of all the different crystal systems, the cubic form possesses the highest symmetry. It possesses nine planes of symmetry, thirteen axes of symmetry (three C_4, four C_3, and six C_2 axes) and one centre of symmetry, i.e. altogether twenty three elements of symmetry.

Crystal lattice : A lattice is defined to be an infinite set of points that are repeated regularly through space. A set of points repeated at a fixed distance along a line is an one-dimensional lattice. [Fig. 5(a)]. A set of points occuring regularly in a plane represent a two-dimensional lattice. Figure 5(b) represents a two-dimensional lattice consisting of a network of rectangles. The lengths of the sides of the rectangles '*a*' and '*b*' are known in crystallography as *primitive translations*. Any displacement from one point to any other point in this lattice can

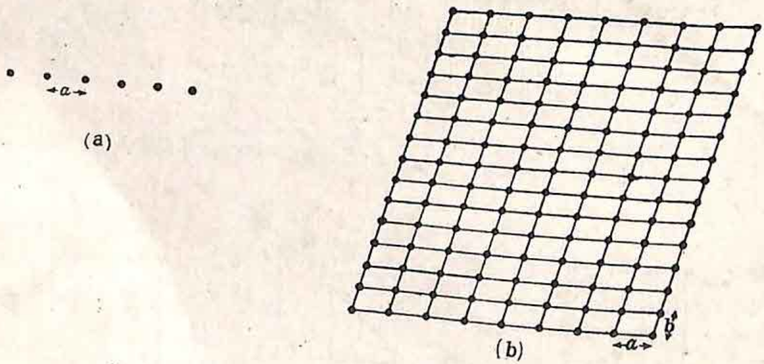


Fig. 5(a),(b). Crystal lattice

be expressed in terms of '*a*' and '*b*' and the angle between the sides represented by '*a*' and '*b*'. Any definite pattern regularly printed on a plane paper is an example of a two-dimensional lattice.

When the method followed in two-dimensions is extended in three-dimensions, a **space lattice** is generated. A space lattice or **unit cell** is thus defined as **an array of points showing how molecules, atoms or ions are arranged at the different sits in three-dimension.** An array of points present in a three-dimensional space lattice is shown in Fig. 5(c). Each point represents an atom or ion. The lattice points can be broken up (divided) into a number of **unit cells.** This may be done, as shown in Fig. 5(c), by connecting the points by a regular network of lines as shown in the figure. An unit cell is the smallest structural unit in the space lattice, which is repeated over and over again to constitute a crystal of a crystalline solid. An unit cell is represented by the portion bounded by bold lines in Fig 5(c). In order to describe an unit cell, the distances *a*, *b* and *c*, which represent the lengths of the edges of the unit cell and the angles α, β and γ, which give the angles between the three axes *OX*, *OY* and *OZ*, are required.

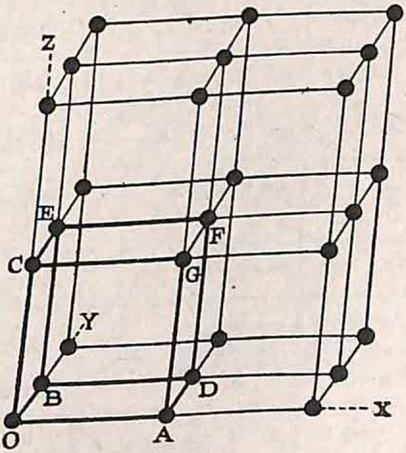


Fig. 5(c)

Classification of crystals : crystal classes and crystal systems.

The overall structure of the crystal bounded by a definite number of faces in a definite pattern is called the **form** of a crystal. A cube is bounded by six faces, while an octahedron is a combination of eight faces in definite pattern. Thus, the cube and the octahedron are two **forms** of crystals. Depending on the individual elements of symmetry, all forms can be classified into thirtytwo **classes** or **point groups**, each of which has the same elements of symmetry. In other words, each form has the same planes, same axes and the same centre of symmetry. Altogether thirty two forms of crystals can exist.

System : Depending on the axes of reference representing their faces, the thirty two forms can be grouped into **seven systems**. The crystals of a particular system have the same ratio of the intercepts on the three crystallographic axes (axial ratio) and the same angle between the three axes (axial angle). But, they may differ in form, size and elements of symmetry. For example, the octahedron and a cube belong to the same system. The octahedron is a cube with exclusive growth of the (1 1 1) plane.

Major characteristics of all the seven systems are given in Table 1. The axial angles are denoted by α, β and γ and the intercepts of the crystallographic axes are given as a, b and c.

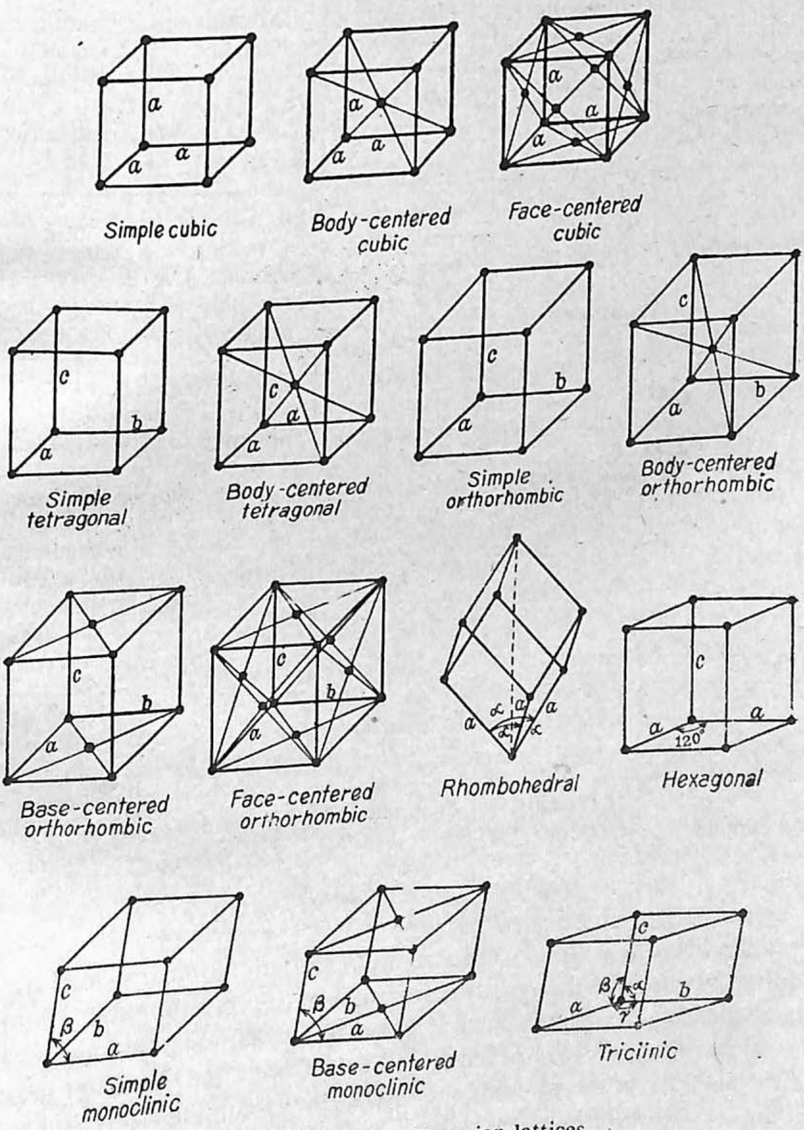
TABLE 1

Axes	Angles	System	Examples
$a=b=c$	$\alpha=\beta=\gamma=90°$	Cubic	ZnS, NaCl, Cu, CaF_2
$a=b$; c	$\alpha=\beta=\gamma=90°$	Tetragonal	SnO_2, White Sn, TiO_2 (Rutile)
a ; b ; c	$\alpha=\beta=\gamma=90°$	Orthorhombic	Rhombic sulphur, $BaSO_4$, KNO_3
a ; b ; c	$\alpha=\gamma=90°$; β	Monoclinic	Monoclinic sulphur, gypsum
$a=b=c$	$\alpha=\beta=\gamma$	Rhombohedral	Calcite ($CaCO_3$), $NaNO_3$,
$a=b$; c	$\alpha=\beta=90°$; $\gamma=120°$	Hexagonal	BN, graphite, ZnS (wurzite)
a ; b ; c	α ; β ; γ	Triclinic	Blue vitriol ($CuSO_4.5H_2O$), $K_2Cr_2O_7$

Bravais Lattices : From geometrical consideration, Bravais showed that there are only fourteen different ways in which similar points can be arranged in three dimensions. Thus, there can be only fourteen different kinds of lattices which are known as *Bravais lattices*. The different Bravais space lattices occuring in different crystal systems (discussed before) are shown in Fig. 6.

Though the details of the internal structure within the unit cell can vary from one substance to another, each and every crystal must possess one of these lattice structures.

Types of solids : The long-range ordered arrangement of the structural units gives rise to the characteristic properties of solids which are quite different from those of the liquids and the gases. The best method of classifying solids is based on the nature of the forces that bind the constituent units. Thus, solids can be broadly divided into four classes : (i) molecular solids, (ii) covalent solids, (iii) ionic solids and (iv) metallic solids. We can arrive at the same type of classification depending on the nature of the units which occupy the lattice points of an unit cell. The molecular solids are characterised by materials whose structural units are molecules. In the case of the covalent solids, these are atoms ; in ionic solids they are ions, while in the metallic solids, positive metallic ions occupy the lattice points surrounded by a 'sea' of electrons.



Simple cubic

Body-centered cubic

Face-centered cubic

Simple tetragonal

Body-centered tetragonal

Simple orthorhombic

Body-centered orthorhombic

Base-centered orthorhombic

Face-centered orthorhombic

Rhombohedral

Hexagonal

Simple monoclinic

Base-centered monoclinic

Triclinic

Fig. 6. The fourteen Bravaian lattices

Some important characteristics of these four types of crystalline solids given in Table 2.

TABLE 2

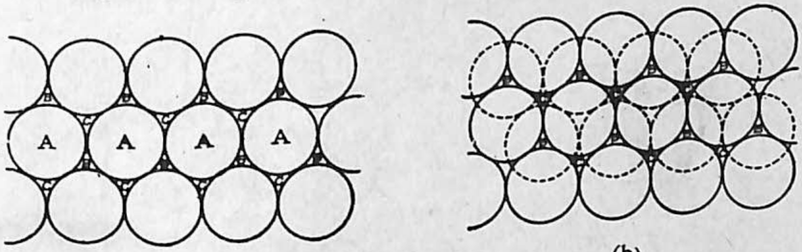
Some important characteristics of various types of crystals :

Characteristics	Molecular Crystals	Covalent Crystals	Metallic Crystals	Ionic Crystals
Units that occupy lattic points	Molecules	Atoms	Positive ions (in sea of electrons)	Positive and negative ions
Binding forces	(i) Van der Waals forces (ii) Dipole-dipole attractions.	Shared electron pair bonds.	Electrostatic attraction between +ve ions and −ve electrons.	Electrostatic attraction between +ve and −ve ions.
Physical properties	(i) Very soft (ii) Low m.p. (iii) Good insulators	Very hard Very high m.p. Non-conductors	Hard or soft Moderate to high m.p. Good corductors	Hard and brittle. Fairly high m.p. Most ionic crystals are non-conductors at ordinary temp. Some (which have crystal defects) behave as semiconductors.
Examples	H_2O (ice) CO_2 (dry ice)	Diamond (C) Quartz (SiO_2) Carborundum (SiC)	Fe, Ag, Cu, Na, K.	NaCl, KNO_3, Na_2SO_4

Packing in solids : On account of their comparatively strong mutual attraction, the constituent units in any crystal lattice, (atoms, molecules and ions) which are taken to be hard spheres, are packed as close as possible to each other. **Closer the packing, greater is the stability of the system,** and this close packing is clearly reflected in the rigidity and low compressibility of the solids. Hence, **one essential feature of the crystalline solids is that the constituent spheres always tend to assume closest packing in three dimensions.** In such a packing, **each sphere is in contact with the maximum possible number of nearest neighbours.**

APPENDIX

First of all let us consider the packing of identical spheres (or different spheres of equal radius) in one plane. Figure 7(a) shows a layer of closest packed spheres in which each sphere (designated by A) is surrounded hexagonally by six nearest spheres in the same plane.



(a)

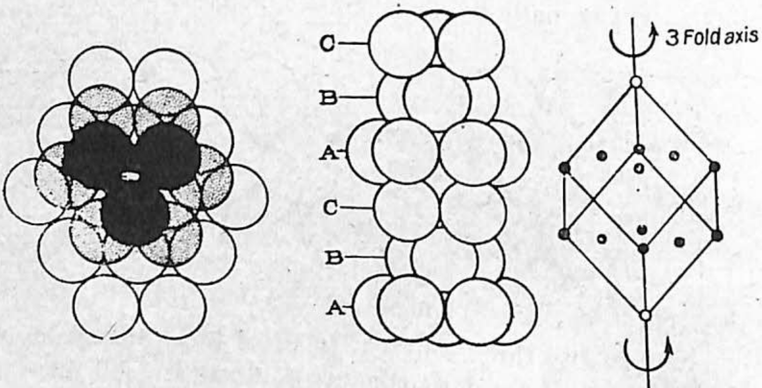
(b)

Fig. 7

We can now visualise three different types of locations in the above layer of spheres which are designated as *A*, *B* and *C*. Of these three, locations *B* and *C* represent two types of **vacancies** or **voids**, triangular in shape. It is to be noted here that the vertices of the triangular 'B'-voids are pointing upwards while the vertices of the 'C'-voids point downwards. Now, a second layer of closest packed spheres can be placed upon the first layer in two different ways ; (i) each sphere occupying a B-void and (ii) each sphere occupying a 'C'-void. It must be appreciated that because of the size of the spheres being considered, both B and C-voids cannot be occupied at the same time. In the case of a single layer of closest packed spheres, the B-voids and the C-voids are identical excepting the directions in which their vertices are pointing and even then, they are interchangeable by turing the layer through 180°. However, they get distinguished after the addition of the second layer as is shown in Fig. 7(b).

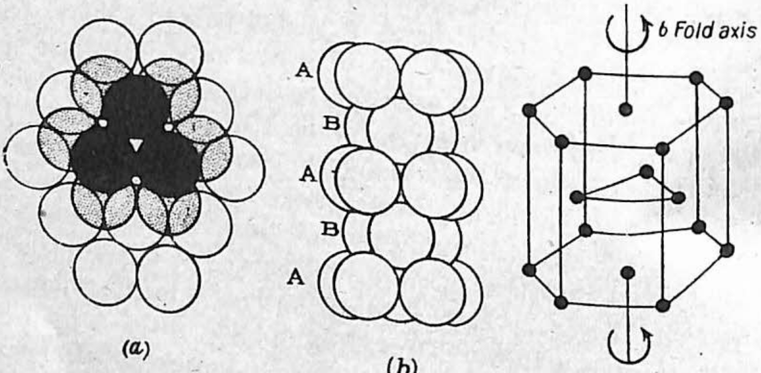
If a third closest packed layer of spheres is now to be placed on the first layer, two different stacking patterns can be visualised. (a) The third layer can be placed with its spheres on the B voids or (b) it can be placed on the 'C'-voids. But now (after the packing of the second layer), the B voids and the 'C'-voids have different surroundings and hence two different types of stacking can occur. If the second layer is packed on the 'B'-voids of the first layer then, one of the available sets of voids for the third layer will be directly above the spheres (disignated by A) in the original first layer. These are the A-sites. The other sets of voids will be the C-voids. Now, if the spheres of the third layer are placed in the 'A'-sites, the stacking order will be ABA. . . On the other hand, if the spheres of the third layer are placed in the 'C' sites, the stacking pattern will be ABC. . . These two stacking sequences can be repeated continuously to arrive at the ABABAB. . . .

and ABCABCABC. . . ., and are called hexagonal closest packing (HCP) and cubic closest packing (CCP) arrangements respectively [Figs. 8(a), (b) and (c) ; Figs. 9(a), (b) and (c)].



(a) (b) (c)

Fig. 8. Hexagonal closest packing



(a) (b) (c)

Fig. 9. Cubic closest packing

A careful inspection of the cubic close packing will indicate that there is a sphere at the centre of each face of the unit cube and hence, the structure is also known as the *face-centred cubic* structure [Fig. 9(c)]. Each sphere in one layer is in contact with six nearest spheres. In addition to this, each sphere is also in contact with three spheres in the layer above and three spheres in the layer below. Thus, the coordination number in the cubic close packed and also in the hexagonal systems is 12. In these two cases, about 74 % of the total space is occupied by the spheres and only 26 % remain void.

Inert gases and several metals crystallise in either hexagonal (Be, Mg, Zn, Cd, Ti, Zr etc.) or cubic closest packed (Cu, Ag, Au, Ca, Sr, Al, Fe, Ni and Pb) arrangements. Solid hydrogen crystallises in the CCP structure, while the hydrogen halides have the HCP structure.

Another possible way of packing spheres is the body centred cubic (BCC) structure. In this arrangement, each of the eight corners of the cubic lattice is occupied by a sphere, while one sphere is placed at the centre of the unit cube. In this system, the co-ordination number of each sphere is 8 and it is not a closest packed structure in which only 68% of the total volume is occupied by the spheres, while 32% space is occupied by voids. In addition to the HCP and the CCP structures some metals (e.g. alkali metals, Ba, V, Mo & Ta) also crystallise in the BCC structure.

Thus, we find that the structures of the molecular solids and metals can be explained on the basis of closest packing of the structural units as discussed above.

Voids or sites in closest packed structures : As pointed out previously, two different types of voids or vacancies generally referred to as "sites" or 'holes', are present in a closest packed solids. When a triangular vacancy between three mutually touching spheres of a closest packed layer has a sphere over it, a **tetrahedral site is created** [Fig. 10(a)]. The sites marked B in Fig. 7(b), represent tetrahedral sites. Thus, the tetrahedral site is a void with four spheres enveloping it and hence, its coordination number is 4.

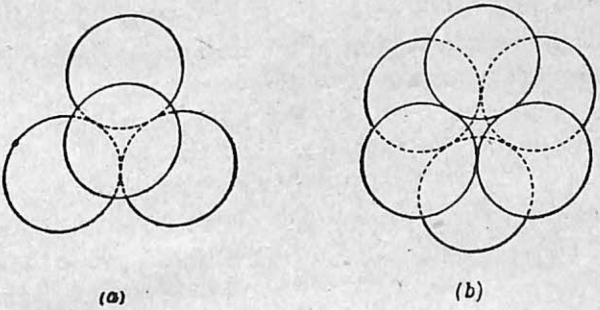


Fig. 10

When a triangular vacancy in a closest packed layer, with its vertex pointing up [sites marked C in Fig. 7(a)] is covered up by a similar triangular vacancy (with its vertex pointing down) present in the next upper layer, **an octahedral site** is created [Fig. 10(b)].

The sites marked C in Fig. 7(b) represent octahedral sites. Such an octahedral site is surrounded by six spheres arranged at the corners of an octahedron and hence, the coordination number of an octahedral site is 6.

The number of a particular type of site (either tetrahedral or octahedral) belonging to one sphere is given by the ratio

$$\frac{\text{number of a particular type of void around a sphere.}}{\text{coordination number of that particular type of site}}$$

Thus, the number of tetrahedral sites belonging to one sphere is given by

$$\frac{\text{number of tetrahedral sites around a sphere}}{\text{coordination number of a tetrahedral site}}=\frac{8}{4}=2.$$

Similarly, the number of octahedral sites belonging to one sphere is $\frac{6}{6}=1$.

So, we find that in a closest-packed structure, the number of octahedral sites is equal to the number of spheres surrounding it, while the number of tetrahedral sites is double that of the number of spheres creating it.

Size of a site or vacancy compared to the sizes of the spheres surrounding it : Let us consider the octahedral sites first. The size of an octahedral site depends on the size of the spheres surrounding it and their relationship with each other can be easily understood with help of the following figure (Fig. 11).

Fig. 11 represents a section of an octahedral site surrounded by four spheres. Let us assume that this vacant site is occupied by a small sphere touching each of the four spheres. Let the centre of this small sphere A, be joined to the centres B and C of two large spheres. Now, AD is perpendicular to BC, where D is the point of contact of the two large spheres. Let the radius of the small sphere be denoted by r_1 and that of the larger spheres (which are taken to be of equal size) be r_2.

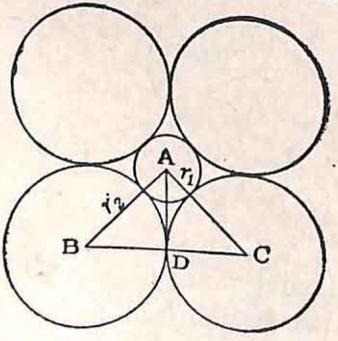


Fig. 11

Then, $AD=BD=r_2$ and $AB=r_1+r_2$

Since, ABD is a right angled triangle,

$$AB^2=AD^2+BD^2.$$

$$\text{or, } (r_1+r_2)^2=r_2^2+r_2^2=2r_2^2$$

$$\therefore\ (r_1+r_2)=\sqrt{2}r_2=1.414r_2$$

$$\therefore\ r_1=1.414r_2-r_2=0.414r_2$$

$$\text{or, } \frac{r_1}{r_2}=0.414.$$

Thus, the size of an octahedral site is about 41% (i.e. less than half) of the size of the surrounding spheres.

In a similar way, it can be shown that the size of a tetrahedral site is only 0.225 (22·5%) of the size of the surrounding spheres.

From the above discussions we can make the following conclusions :

(a) For each sphere of a close-packed arrangement, two tetrahedral and one octahedral sites are present.

(b) An octahedral site is larger than a tetrahedral site. The size of both these sites depends on the sizes of the surrounding spheres and increases with the increase in size of these spheres.

Structure of ionic solids and other crystalline substances, where the units occupying lattice points are spheres of unequal radii: In an ionic solid, the cations are surrounded by the anions and *vice-versa*, in a close-packed manner. In most cases, the cations and anions are of unequal radii, the cationic radius being much smaller than that of the anion in general. Such is also the case with atoms of unequal atomic radii. In all such crystals, the coordination number is related to the sizes of the constituent spheres and is generally considered in terms of the radius-ratio which is defined as

$$\frac{\text{radius of the cation}}{\text{radius of the anion}} = \frac{R^+}{R^-}.$$

In an ionic compound AX, if the coordination number is three, three X^- ions are in contact with the cation A^+ touching each other, or without mutually touching. The state of affairs, when the three X^- ions are not touching each other, is shown in Fig. 12(c). Here, the force of attraction between the cation and the anions is quite strong because of their mutual contact with each other. At the same time, because the anions are separated from each other, the anion-anion repulsion is rather small. Hence, such a structure is quite stable. But, in a closest packed arrangement, when all the four spheres are in contact with each other (Fig. 12(b)], it can be shown from geometrical considerations that, the ratio $\frac{R^+}{R^-}$ is equal to 0.155. This radius-ratio

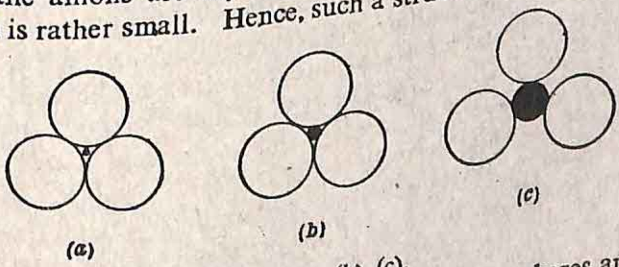

(a) (b) (c)

Fig. 12(a), (b), (c).

is the limiting value for the existence of such a crystalline solid structure. If the radius-ratio falls below 0.155, the cation A^+ will not fit tightly and is said to "rattle" in the lattice [Fig. 12(a)] and the structure is unstable. The situation represented in Fig. 12(b) is less stable than that shown in Fig. 12(c) because of the increase in the anion-anion repulsion due to mutual contact of the X^- ions. Coordination numbers of common occurrence are 3, 4, 6, and 8 and the limiting radius-ratio for the stablest arrangement in each case can be calculated. These data are given in the table below along with the shape of the resultant structural units.

Cordination number	Shape	Limiting radius-ratio
3	Plane triangle	0.155—0.225
4	Terahedral,	0.225—0.414
	Square plane	0.414—0.732
6	Octahedral	0.414—0.732
8	Body-centred cubic (bcc)	0.732—1.00

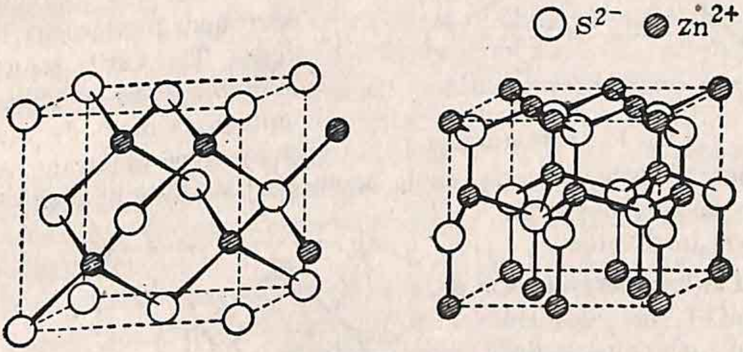
As pointed out previously, in a close-packed arrangement of spheres, two different types of holes, are present. The tetrahedral holes are surrounded by four spheres, while the octahedral holes are enclosed by six spheres. In a close-packed arrangement, for each constituent sphere there will be two tetrahedral holes and one octahedral hole. Thus, the number of tetrahedral holes per sphere is double the number of octahedral holes. The size of the octahedral holes, however, is larger.

In an ionic compound, when the larger ions (generally anions) are close-packed, the smaller ions (generally cations) will occupy the holes present. Thus, they may occupy either tetrahedral holes or octahedral holes. Generally, the type of holes that the smaller ions will occupy depends on their sizes and it can be predicted from the knowledge of the *cation : anion radius-ratio*. Hence, a coordination number of four is attributed to an ion occupying a tetrahedral hole, and an ion occupying an octahedral site has a coordination number of six.

Structure of ionic compounds of the type AX :

Three different structural arrangements, widely found among the compounds of this type, are represented by the structures of zinc sulphide, sodium chloride and cesium chloride.

Let us consider zinc sulphide first. The ionic radius of Zn^{+2} is 0·74Å and that of S^{2-} is 1·84Å. Thus, the Zn^{+2} : S^{2-} radius-ratio is 0.40. From the table containing the values of radius-ratio and the consequent shape of the structural unit, we can clearly see that in ZnS, each Zn^{+2} will be tetrahedrally surrounded by four S^{2-} ions and each S^{2-} ion is similarly surrounded by four Zn^{+2} ions. As the coordination numbers of both the cation and the anion is 4, it represents a 4:4 arrangement. Zinc sulphide exists in two different forms known as Zinc blende and Wurtzite, both having 4:4 arrangements. These two structures are represented below [Fig. 13(a) and (b)].



(a). **Zinc blende,** Fig. 13 (b). Wurtzite

In both these arrangements, the S^{2-} ions (the larger ions) exist in close-packed conditions and the Zn^{+2} ions (the smaller ions) occupy tetrahedral sites in the crystal lattice. As already pointed out, there are two tetrahedral holes for each S^{2-} ions and as zinc sulphide has a formula of ZnS, only half of the tetrahedral sites are occupied by Zn^{+2} ions. Actually, every alternate tetrahedral hole is occupied. The zinc blende form is related to *close-packed cubic structure*, while the Wurtzite form belongs to the *hexagonal close-packed system.*

Rock-salt (NaCl) type structure : The radius-ratio of Na^+ : Cl^- is 0.52 and hence NaCl will have an octahedral arrangement in which each Na^+ ion is surrounded by six Cl^- ions remaining at the corners of a regular octahedron. Each Cl^- ion is similarly surrounded by six Na^+ ions and hence it is a 6:6 arrangement. The structure of NaCl is given in the margin (Fig. 14).

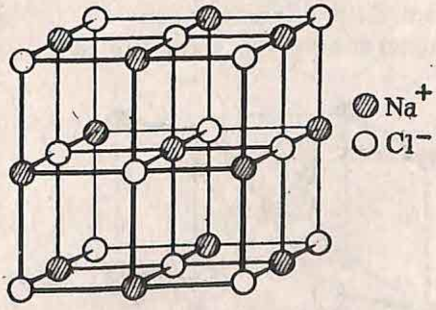


Fig. 14. Rock salt (NaCl)

In this arragement, the Cl^- ions are present in the cubic close-packed condition and the Na^+ ions occupy the octahedral holes. Thus, rock salt structure belongs to the *cubic close-packed system*.

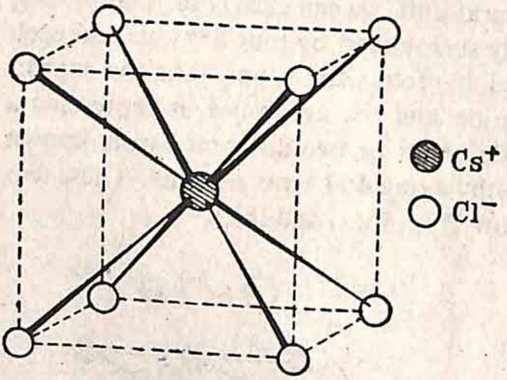


Fig. 15. CsCl structure

The CsCl structure : In CsCl, the radius-ratio of 0.93 points to a *body-centred cubic type* arrangement, in which each Cs^+ ion is surrounded cubically by eight Cl^- ions and each Cl^- ion is similarly surrounded by eight Na^+ ions. The CsCl structure is represented in Fig. 15 and it is a body-centred cubic type of arrangement, but not strictly body-centred cubic, because in CsCl the ions at the body-centre and the ions at the corners are different.

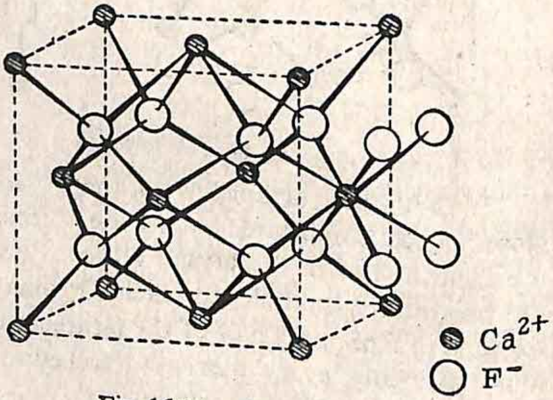


Fig. 16 (a). Fluorite structure

Lattice energy of a crystal : For detailed discussions on lattice energy, its significance, calculation of lattice energies using Born-Haber cycle, important characteristics of ionic compounds, role of lattice energy and solvation energy in determining the solubility of ionic compounds in polar solvents, see Vol. I, Ch III, pp. 134—140.

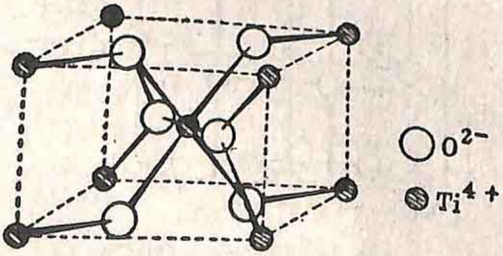


Fig. 16 (b). Rutile structure

Structure of compounds of the type AX_2 : Two very common structures in which AX_2-type compounds occur are the fluorite (CaF_2) structure and the rutile (TiO_2) structure. These structures are given in Figs. 16 (a) and (b).

The Fluorite structure : In CaF_2, the cation-anion radius-ratio is

0.73 and hence, it should belong to the body-centered cubic arrangement. In it, each Ca^{+2} ion is surrounded by eight F^- ions in a body-centred manner. Since, the formula of calcium fluoride is CaF_2, for each Ca^{+2} ion two F^- ions are present and hence, the coordination number of the two ions are different. Each F^- ion is tetrahedrally surrounded by four Ca^{+2} ions. Since the coordination numbers of Ca^{+2} and F^- are eight and four respectively, this is a 8:4 arrangement. The fluorite structure is shown in Fig. 16(a).

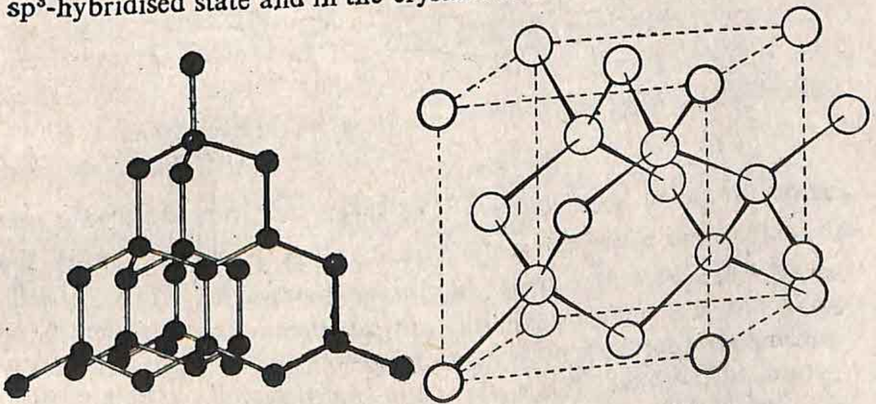
AX_2-type compounds of the dioxide and difluoride class, having a radius-ratio equal to or greater than 0.73, generally possess the fluorite structure.

The Rutile structure : In titanium dioxide, TiO_2, the radius-ratio is 0.486. Here, the coordination number of Ti^{+4} is six and that of O^{2-} is three. Each Ti^{+4} ion is surrounded by six O^{2-} ions placed at the corners of a distorted octahedron and each O^{2-} ion have three Ti^{+4} ions arranged in a plane-triangle around it. It is not a close-packed arrangement. The rutile structure is shown in Fig 16 (b).

The rutile structure occurs when the radius-ratio lies between 0.73 and 0.41.

Structures of covalent crystals : In the crystal lattice of a covalent crystal, the lattice points are occupied by atoms linked with each other by a continuous system of *shared electron-pair bonds*. Diamond, graphite and carborundum are the most familiar examples of covalent crystals.

Structure of diamond : In diamond, the carbon atoms are in the sp^3-hybridised state and in the crystal lattice of diamond, each carbon atom is tetrahedrally bonded to four other carbon atoms. The structure of diomond is given in Fig. 17.1. From this figure, it is clear



(a) (b)

Fig. 17·1 (a) and (b)

that each carbon atom is at the centre of a tetrahedron, linked with four other carbon atoms occupying the four corners of the tetrahedron, utilising sp^3-hybrid orbitals. Such a structure is extended throughout the entire crystal in three dimensions, as a result of which, the crystal is a giant molecule or a *huge three-dimensional polymer*. Since such covalent bonds are very strong and have strong directional character, diamond is very hard, high-melting and extremely difficult to deform. Because of the complete pairing and localisation of all the electrons at the C—C covalent bonds, diamond is a non-conductor of electricity.

Structure of graphite : Graphite is a *two-dimensional polymer*. In graphite, the carbon atoms are in the sp^2-hybridised state, and of the four valence-electrons of carbon, three (occupying the three coplanar sp^2-orbitals) are utilised for bonding. It has been found that in graphite, the carbon atoms are arranged in regular hexagons (like benzene rings) fused together as shown below (Fig. 17·2). Such type of crystal lattices are called *layer lattices*. The sheets or layers are placed one above the other at a distance of 3.35Å, the C—C bond distances in the hexagon being 1.415Å. This rather large distance of 3.35Å between two layers rules out the possibility of the formation of a covalent bond utilising the fourth electron of each carbon atom occupying the unhybridised p-orbital. Thus, *the fourth valence-shell electron remains free and it is this electron, which is responsible for the good electrical conductivity of graphite*. Due to the large distance between the two adjacent sheets, the force operating between them are of weak van der Waal type. It is due to the weakness of this force that two such layers

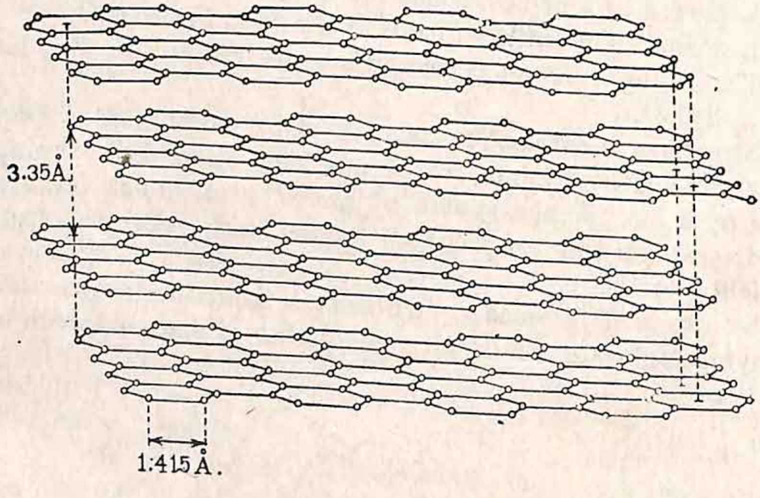


Fig. 17·2

can slide over each other by the application of a tangential force, which is the reason of its lubricating property and greasy feeling. The wide separation of the layers also accounts for the lower density of graphite compared to that of diamond and also explains why graphite is quite soft and cleaves easily between the layers.

Structure of metallic crystals : Apart from a very few exceptions, most of the metals belong to the following three type of close-packed structures, already discussed. The table given below indicates the structure-type and coordination number of some metals.

Crystal lattice	Metals	Coordination number
Cubic close-packed (ccp)	Cu, Ag, Au, Ca;Sr,Al,Fe,Ni,Pb	12
Body-centred cubic (bcc)	Li, Na,K,Rb,Cs,Ba,V,Mo	8
Hexagonal close-packed (hcp)	Be,Mg,Zn,Cd,Ti.Zr,Os	12

From this table we can clearly see that, (i) the coordination numbers of the metal atoms are 8 or 12, i.e. each atom is associated with 8 or 12 atoms. We also know that, (ii) the metals have smaller ionization energy than the other elements (with the exception of mercury) and (iii) the number of valence-electrons are small and less than the number of orbitals in the valence-shell. From these three considerations, it becomes evident that the atoms of the metallic elements cannot be held in the crystal lattice by covalent bonds, as they do not have the required number of electrons in their valence-shell. The atoms occupying the lattice points of a metallic crystal, therefore, are held to each other by means of a special type of bond, known as *metallic bond.*

For the rest of the discussion on metallic crystals and metallic bond, see Vol. I, Ch. III, pp. 173—174.

Defects or imperfections in crystals : The most important and characteristic feature of the crystalline solids is the completely regular three-dimensional pattern in which the constituent atoms, ions or molecules are arranged. Defects or imperfections in a crystal are generated by deviation from the regular and periodic arrangement inside the crystal lattice. Defects in solids may be conveniently divided into two broad classes.

(a) **Stoichiometric Defects :** Defects in compounds where the numbers of cations and anions are in the exact ratios indicated by their chemical formulae.

(b) Non-stoichiometric defects or defects in non-stoichiometric compounds.

Stoichiometric defects or thermodynamic defects : Two different types of such defects are observed, which are known as **Schotky defects** and **Frenkel defects.** These are now discussed one by one.

Schotky defects : If one positive and one negative ions are absent from a crystal lattice, a pair of so called '*holes*' are generated in that lattice. Such a situation is depicted in Fig. 18, where a pair of B^- and A^+ ions are missing from the crystal lattice whose positions are indicated by empty circles. Highly ionic compounds with a high coordination number, in which the positive and negative ions are of comparable radii, have a tendency to form Schotky defects. CsCl is such an example ($r_{Cs}{}^{+}=1.67\text{Å}$ and $r_{Cl}{}^{-}=1.81\text{Å}$).

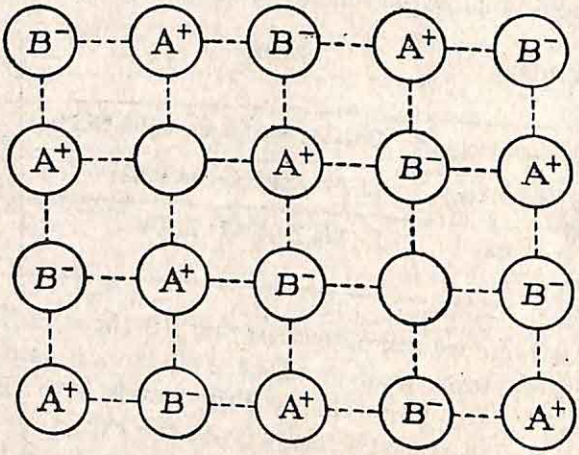


Fig. 18. Schotky defects

Frenkel defects : If an ion is removed from its correct lattice site and put in an interstitial position, a Frenkel defect is generated. Such a situation is represented in Fig. 19. Here, the cation A^+ is dislocated from its correct lattice position indicated by the empty circle and thereby creating a 'hole' in the crystal lattice. As positive ions are usually smaller than the anions, the positive ions are commonly found to occupy interstitial positions. Frenkel defect tends to be formed in compounds in which there is a large difference in the cation and the anion radii, the cation being smaller. These compounds possess considerable covalent character due to the strong polarisation of the large anions by the small cations as predicted by Fajan's rules of ionic distortion (see Vol. I, Ch. III,

p. 169-172). Formation of Frenkel defects is also favoured in compounds of low coordination number, as fewer attractive forces are to be broken in such compounds to remove an ion from its correct lattice position. Examples of Frenkel defects are found in ZnS and AgBr.

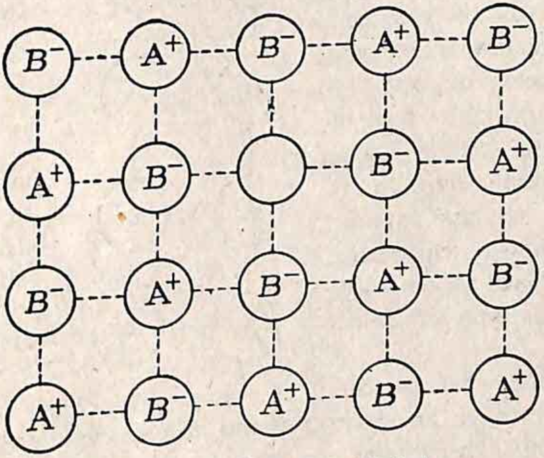


Fig. 19. Frenkel defect

A crystalline solid possessing defects may conduct a small amount of electricity by ionic mechanism. Under a suitable potential difference, an ion may move from its proper lattice position to a hole and thereby create a new hole. In this way a 'hole' may migrate across a crystal which amounts to the movement of a charge in the opposite direction.

As the number of these defects tends to increase with temperature, they are also known as 'thermodynamic defects'. Thus, conductivity of such solids increase with temperature.

Non-stoichiometric defects : Non-stoichiometric compounds exist over a range of chemical compositions and the ratio of the anions and cations differs from that indicated by the chemical formula, and the negative and the positive charges are balanced by having extra electrons or positive charges incorporated in the lattice. Thus, such solids have irregular structures, containing inherent defects, along with the Schotky and Frenkel defects discussed before. Non-stoichiometric defects are conveniently divided into two categories :

(i) *Metal excess and* (ii) *metal deficiency.*

Defects due to metal excess : In the crystal lattice of a compound, metal excess can be generated in two ways. (i) By the absence of an anion from its lattice site and forming a 'hole' which is occupied by an electron to maintain charge balance as is shown in Fig. 20 (a).

Such a defect is similar to the Schotky defect in that, there are 'holes' and not interstitial ions. But the difference lies in the fact that, in place of a pair of 'holes' in a Schotky defect, only one hole is present here and that too is occupied by an electron. Crystals which have a tendency to form Schotky defects also tend to form this type of defect due to metal excess. When sodium chloride is heated with sodium vapour, a yellow non-stoichiometric variety of NaCl is obtained, in which this type of defect is found.

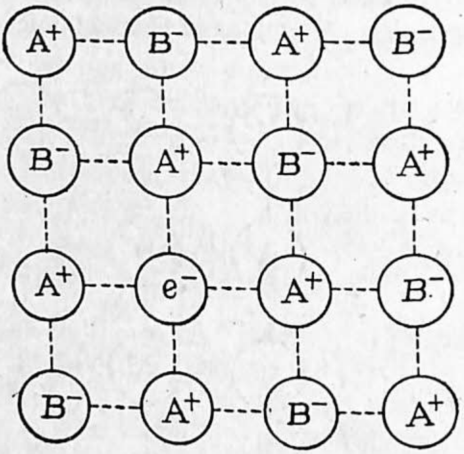


Fig. 20(a)

Metal excess defects can also be formed if an extra positive ion occupies an interstitial position in the lattice, the charge-balance being maintained by accomodating an extra electron in another interstitial position as shown in Fig. 20(b). This kind of defect due to metal excess is more common than the first type, and an example of this kind is ZnO. This kind of defect resembles Frenkel defects in that, there are ions in the interstitial positions and no 'holes' are there. But it must be noted that electrons are also there.

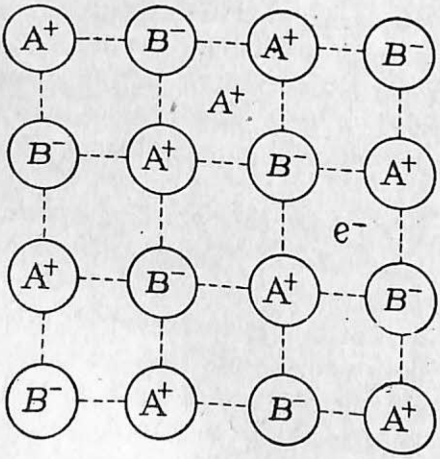


Fig. 20(b)

It is quite clear that crystals with either of these defects may conduct electricity due to the presence of free electrons in the lattice. However, the number of such defects being very small, the conductivity will be very small compared to the electronic conductors like metals and electrolytic conductors like fused salts and salt solutions. As the mobility of the free electrons increases with temperature, such materials exhibit increase in conductivity with the increase in temperature. These materials are called **semiconductors of the n-type,** since conduction in this type of semiconductors is due to the movement of negative charge in the form of electrons.

Metal deficiency : The necessary condition for metal deficiency to occur is the existence of the metal in variable valency states. Such metal deficiency, in principle, may occur in two ways: (i) In this way, a positive ion is absent from its proper lattice position and the charge-balance is maintained by an adjacent metal ion having an extra unit of positive charge as shown in Fig. 21(a). Examples of such defects are found in FeO, FeS and NiO; (ii) The other way to create metal deficiency is to have an extra anion, (B^-) in an interstitial position, with the charge-balance maintained by an extra positive charge on an adjacent cation (A^{+2}) as shown in Fig. 21(b). However, no such example is known up till now. Crystals with such metal deficencies behave as semiconductors, because the movement of an electron from an A^+ to form an A^{+2} ion is an apparent movement of A^{+2}, which is regarded as the movement of a positive 'hole', and substances in which conduction takes place due to this type of movement are known as **p-type semiconductors.**

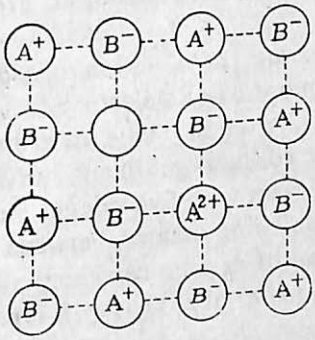
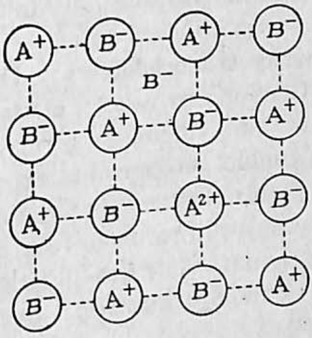


Fig. 21(a)



(b)

Semiconductors and transistors : Depending on the magnitude of their electrical conductivity, solids can be broadly divided into metals, semiconductors and insulators. The metals can have a conductivity as high as 10^8 ohm^{-1} cm^{-1}, while an insulator may possess the lowest conductivity value of 10^{-22} ohm^{-1} cm^{-1}. Semiconductors behave as insulators at absolute zero but conduct electricity at room temperature or above by the migration of electrons or 'holes' or other charge-defects. Thus, semiconduction in solids arises out of the presence of impurities and various types of defects discussed previously.

Silicon and germanium are the most common and widely used semiconductors. Belonging to the Gr. IVB of the periodic table, both of them have four valence electrons which form four covalent bonds with the atoms of other elements, generating a tetrahedral diamond-like structure. If sufficient energy is supplied to a silicon or germanium crystal, some of the bonds may break and electrons may be ejected from their normal sites in the lattice. These electrons can migrate across the crystal, leaving a positive 'hole' at the site of bond-breakage. Electrical conduction in a silicon or germanium crystal can take place by the movement of an electron in one direction and the migration of the positive 'hole' in the other. Such materials are known as **intrinsic semiconductors.**

Impurity semiconductors : Deliberate introduction of some impurities (having one valence electron more or one electron less than Si or Ge) to pure silicon or germanium, gives rise to a new and more efficient conduction known as **extrinsic conduction.** Thus, an addition of a few atoms of arsenic (a Gr. VB element with five valence electrons) in germanium will result in four bonds being created between arsenic and germanium, while the fifth electron of arsenic can carry current in terms of a moving electron. Such a material is thus a **n-type semiconductor.**

If now, an element like indium, (Gr. IIIA element), with three valence electrons, is added to either Si or Ge, it can form only three bonds and create 'positive hole', as some sites, normally occupied by electrons (if the impurity had four valence electrons) are left vacant. Under applied potential, electrons from adjacent sites may fill these 'positive holes' and leave behind other such 'holes'. Thus, by the migration of such holes across the crystal, the current is carried. It is quite evident that such materials fall in the class of **p-type semiconductors.**

Junction-semiconductors : By carefully controlled introduction of different types of impurities, single crystals can be prepared in such a manner that one part of it is an *n*-type and the other part is a *p*-type, creating an *n-p* junction. This *n-p* junction allows a current input to flow in one direction only and hence behaves as a rectifier. The junction-type semiconductors are popularly known as **transistors.** Transistors with three junctions like *n-p-n* and *p-n-p* are being used in radio, television and other electrical circuits.

The Bragg method of structure determination by X-ray deffraction : When a beam of homogeneous X-rays is allowed to fall on a crystal, the X-rays are scattered by all the atoms in the crystal. The radiation scattered by each and every atom interferes with the radiation scattered by all the other atoms. This is similar to the interferene pattern observed in the case of a light beam falling on a deffraction grating, where the light scattered by each line interferes with the light scattered by all other lines. When a group of atoms is arranged in an orderly fashion along a plane of a crystal, the interference pattern of the scattered radiation is in the form of a plane wave, just as if the radiation had been reflected from a plane mirror. But there is an essential difference between the ordinary reflection of light and X-ray deffraction, in that interference (in the case of X-rays) takes place at certain angles, whereas reflection can take place at any angle. The Bragg method of determination of structure of crystalline solids is based on this property of interference by planes of atoms.

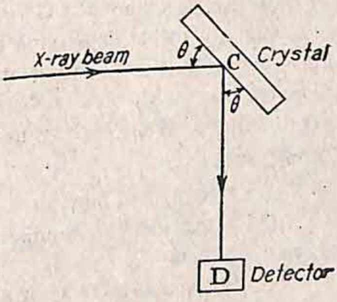


Fig. 22(a)

The experimental set up of this method is shown schematically in Fig. 22(a). The crystal being examined is mounted on a rotating device as also is the detector. The crystal is so placed that the angle of incidence equals the angle of reflection, and the detector is placed in a position to receive the reflected ray. As X-rays can penetrate deep into the crystal, the reflections occur from a number of parallel planes [two of which are shown in Fig. 22(b)], and only when the reflections from these planes interfere constructively, the detector D receives detectable signal. The condition for constructive interference is indicated in Fig. 22(b) which represents reflections from two successive planes placed at a distance '*d*'. Under these conditions, the extra distance travelled by the ray reflected from the second plane is $2d \sin\theta$ and this must be an integral multiple of the wavelength of the X-ray used. Thus, we can write the eqn.

$$n\lambda = 2d \text{ Sin } \theta.$$

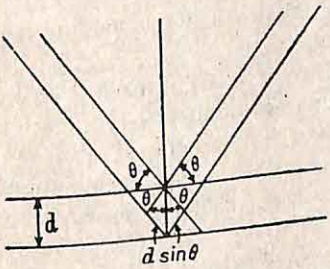


Fig 22(b)

This is the Bragg reflection law. From the knowledge of λ (which one can select according to convenience) and the values of θ for constructive interference (which can be read from the scales attached to the detector and the crystal support), the values of *d* can be computed. These *d*-values or inter-planar spacings are essential characteristics of a crystal and are determined by the size and the geometry of arrangement of the lattice constituents. X-ray deffraction patterns can thus be readily used for the identification of substances, or for analysing individual components of a mixture.

MODEL QUESTIONS

1. (a) Explain how solids differ from liquids and gases.

(b) Distinguish between crystalline and amorphous solids.

2. (a) What are crystalline solids ? Explain the utility of the concept of crystallographic axes, and express it in the form of Hauy's Law of rational intercepts.

(b) What are the Miller indices of the planes denoted by the intercept-ratios 2:1:2 and $\infty : 1 : \infty$. and $1 : \frac{1}{2} : \infty$? What is the intercept-ratio made by a plane designated by the Miller indices $(\bar{1}\ 1\ 1)$?

3. What is meant by the elements of symmetry of a crystal ? Describe the different elements of symmetry of a cubic crystal.

4. Define space lattice. What are the seven systems into which the different forms of crystals can be grouped ? Give the names of the fourteen Bravais lattices.

5. Classify solids depending on the nature of forces that bind the constituent units and point out some important characteristics of each of them.

6. Discuss, with clearly drawn figures, the close-packing of the constituent units in solids. What is the difference between hexagonal close-packing and cubic close-packing ?

7. (a) Distinguish between a tetrahedral site and an octahedral site ?

(b) What are the numbers of tetrahedral sites and octahedral sites per sphere in a crystal ?

(c) Show that the size of an octahedral site is about 41% of the size of the surrounding spheres.

(d) Show that the size of a tetrahedral site is about 22.5% of the size of the surrounding spheres.

8. Explain radius-ratio effect in ionic crystals. Discuss how the stability and shape of an ionic lattice is controlled by the radius-ratio.

9. Discuss the structures of the AX type ionic compounds with reference to zinc sulphide and sodium chloride. Draw clear diagrams to illustrate your answer.

10. Draw clear diagrams and discuss the fluorite and rutile structures.

11. Discuss the structures of covalent crystals with reference to diamond and graphite. On the basis of these structures explain the widely defferent properties of the two allotropic modifications of carbon.

12. Discuss the more important physical properties of metals. Attempt an explanation of these properties on the basis of structure of metals.

13. Explain the term 'lattice energy'. How would you proceed to calculate the lattice energy of NaCl ? Why is the 'lattice energy' of an ionic crystal so high ?

14. Explain what is meant by (a) Schotky defect and (b) Frenkel defect with suitable illustrations.

15. What is meant by a non-stoichiometric defect ? Explain the cases of (a) defects due to metal excess and (b) defects due to metal deficiency. Give appropriate examples.

16. What are semiconductors ? Explain, with examples, how n-type and p-type conduction occurs. What is meant by a junction semiconductor ?

17. Discuss the principles of the Bragg method of structure determination by

X-ray deffraction of single crystals with a schematic diagram of the experimental set up.

Objective type

17. Answer by *yes* or *no*.

(a) Isotropy is characteristic of an amorphous solid, while anisotropy is generally associated with the crystalline state.

(b) Of all the crystal-systems the cubicform possesses the highest symmetry.

(c) The structure of sodium chloride belongs to the monoclinic system.

(d) The structure of graphite belongs to the hexagonal system.

(e) The size of the octahedral voids are less than that of tetrahedral voids.

(f) The coordination number of a tetrahedral void is four.

(g) If the radins-ratio R^+/R^- falls below the value of 0.155 in an ionic solid, the structure will be unstable.

(h) If the R^+/R^- ratio lies in the range of 0.732-1.00, the solid ionic compound will have a body-centred cubic shape.

(i) A n-p-type semiconductor can act as a rectifier.

18. (a) Depending on the individual elements of symmetry, all forms can be grouped into thirty two——or——.

(b) Depending on the axes of reference representing their faces, the thirty two forms can be grouped into seven——.

(c) There can be only fourteen different types of lattices which are known as——

(d) The wurtzite structure of ZnS belongs to the ——system.

(e) In covalent crystals, the binding force comes out of——

(f) The coordination number of an octahedral void is——.

(g) The junction-type semiconductors are popularly known as——.

(h) Semiconductors conduct electricity at room temperature or above by the migration of——or other——defects.

19. Tick the correct answer:

(a) In ionic crystals, the binding force is (i) Van der Waals forces, (ii) shaired electron pair bonds, ('ii) electrostatic attraction between +ve and −ve ions, (iv) dipole-dipole attractions.

(b) Octahedral voids are (i) smaller, (ii) equal to, (iii) larger than tetrahedral voids.

(c) The radius ratio (R^+/R^-) of 0.225—0.414 will give rise to a shape of (i) octahedron, (ii) tetrahedron, (iii) plane triangle, (iv) square plane,

(d) A Schotky defect is created due to the removal of (i) positive ion (ii) a pair of +ve and -ve ions (iii) a negative ion, from the crystal lattice.

(e) A Frenkel defect is generated by (i) complete removal of an ion from the crystal lattice, (ii) by the removal of one ion from its correct lattice position and placing it in an interstitial position, (iii) complete removal of a pair of ions from the crystal lattice.

about the book

This is the first published book on *General and Inorganic Chemistry*, written according to the new syllabi of different Universities for the B.Sc. students. The main aim of the authors of this publication is to bring this relatively complex subject within easy grasp and understanding of the beginner students who are preparing themselves for B.Sc. degree with Chemistry, both in the Pass and the Honours course. Being associated with the University examinations in Chemistry in the graduate and higher levels for more than 15 years, the authors have gathered enough experience regarding the real deficiencies and drawbacks of the students in mastering the subject. They have, therefore, spared no pains to present the subject-matter of the book in a lucid, attractive and easy-to-understand manner, so that the erstwhile difficulties of the students are removed and they learn the subject with pleasure. We have no doubt that this book will be a real boon to the students.

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